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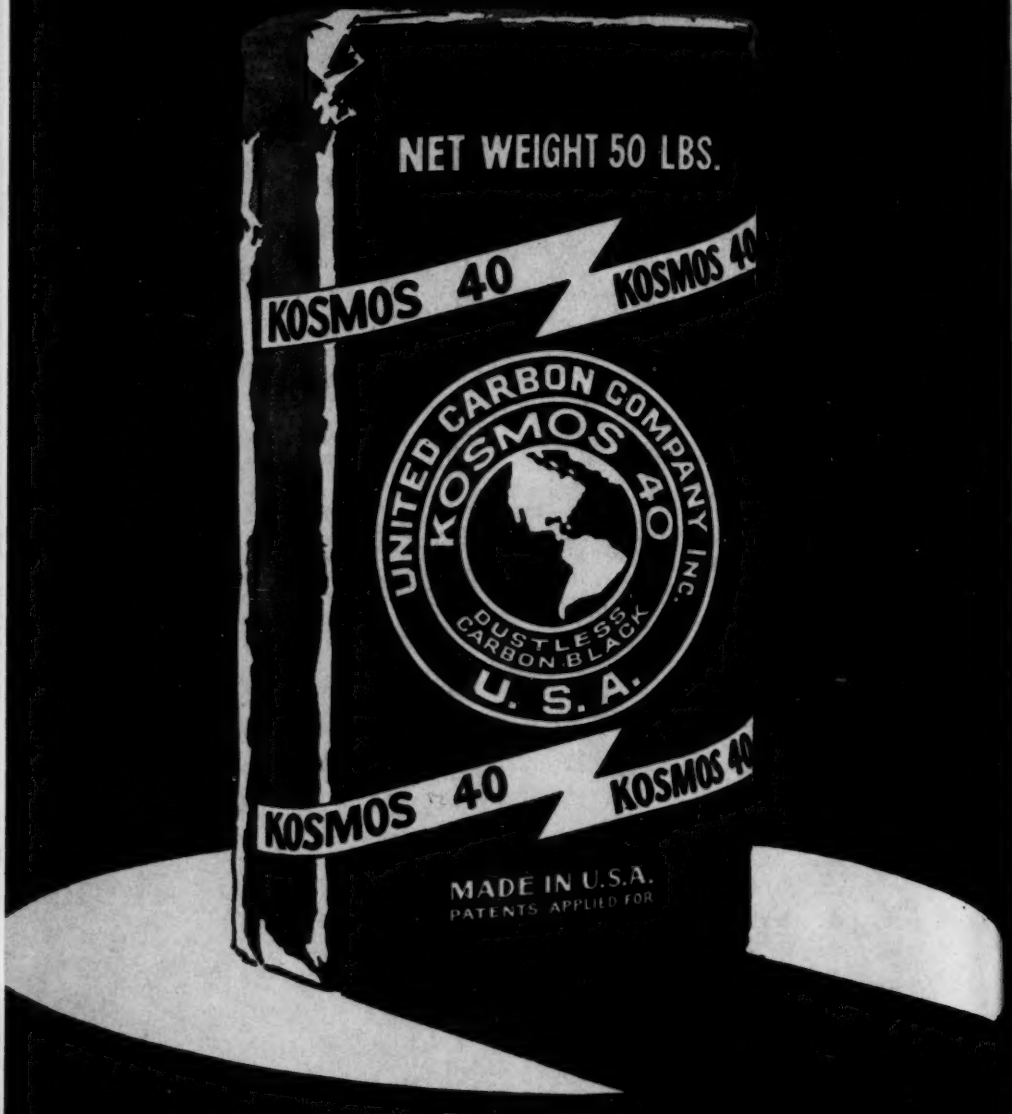

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Vol. XXII **April, 1949** **No. 2**

CONTENTS

General Section PAGE

Officers iii
The Connecticut Rubber Group: Its History v
New Books and Other Publications vi

Reprinted Papers

The Unsaturation of Butadiene Rubbers. A. A. VASIL'EV 287
The Abnormal Melting of Raw Rubber. AKIRA ISIHARA 299
Structural Changes in Rubber Brought about by Molecular Oxygen. III. Properties of Disintegrated Vulcanized Natural Rubber. B. DOGADKIN, Z. TARASOVA, and A. PASYNSKII 310
Measurements of Diffusion in Rubber. F. GRÜN 316
The Interaction Between Rubber and Liquids. X. Some New Experimental Tests of A Statistical Thermodynamic Theory of Rubber-Liquid Systems. GEOFFREY GEE 320
Flow Phenomena in Rubber. I. Flow Curves for Natural Rubber. D. W. SAUNDERS AND L. R. G. TRELOAR 333
Polymerization. VIII. The Action of Metalating Reagents on Rubber. AVERY A. MORTON AND HUGH E. RAMSDEN 342
The Reaction of Sulfur and Sulfur Compounds with Olefinic Substances. IV. The Thermal Decomposition of Organic Polysulfides, and its Contribution to the Sulfur Olefin-Reaction. GEORGE F. BLOOMFIELD 348
x-Ray Studies of Low-Temperature Polybutadiene and Butadiene-Styrene Copolymers. KARL E. BEU, W. B. REYNOLDS, C. F. FRYLING, AND H. L. MCMURRY .. 356
Influence of Structure on Polymer-Liquid Interaction. III. Swelling and Mechanical Properties of Some Partly Crystallized Polymers. G. SALOMON 370
Reaction Kinetics of Adiabatic Systems. M. GORDON 378
Adiabatic Reaction Kinetics of Buna-S Vulcanization. M. GORDON 386
Progress in Polymerization Theory of Interest in Synthetic Rubber Production. L. B. MORGAN 392
Refractometric Determination of Second-Order Transition Temperatures in Polymers. IV. Butadiene-Acrylonitrile Copolymers. RICHARD H. WILEY AND G. M. BRAUER 402
Process Problems in Low-Temperature Emulsion Polymerization. J. E. TROYAN . 405
Transport and Equilibrium Phenomena in Gas-Elastomer Systems. I. Kinetic Phenomena. R. M. BARRER AND G. SKIRROW 427

Transport and Equilibrium Phenomena in Gas-Elastomer Systems. II. Equilibrium Phenomena. R. M. Barrer and G. Skirrow 440
The Dynamic Characteristics of Neoprene Vulcanizates. N. L. Catton, E. H. Krismann, and W. N. Keen 450
Effect of Light on Neoprene. I. Discoloration of GR-M Vulcanizates by Direct Sunlight. P. A. Sanders 465
A Study of Electrostatic Charges Produced During Mastication of Rubber and of GR-S. R. S. Havenhill, L. E. Carlson, and J. J. Rankin 477
Physical Properties of Fractions of GR-S and Their Vulcanizates. John A. Yanko 494
Plasticization of Natural and Synthetic Rubbers. II. GR-S. G. H. Piper and J. R. Scott 518
Electrically Conducting Rubber. K. A. Lane and E. R. Gardner 535
Stability of Accelerators as Affected by High Processing Temperatures. F. L. Holbrook and T. H. Fitzgerald 555
Basic Reactions Occurring During Rubber Reclaiming. II. The Influence of Solvent Naphtha, Storage of Reclaim and Aging of Scrap Prior to Reclaiming, and Infrared Spectra of Natural Rubber Reclaim. D. S. Le Beau 560
Analysis of Natural and Synthetic Rubber by Infrared Spectroscopy. H. L. Dinsmore and Don C. Smith 572
Properties of Ebonite. XXXIV. Influence of Organic Accelerators of Vulcanization. D. G. Fisher, R. G. Newton, R. H. Norman, and J. R. Scott 599
Properties of Ebonite. XXXV. Further Experiments on the Influence of Sulfur Ratio. J. R. Scott 609

RUBBER CHEMISTRY AND TECHNOLOGY

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THE UNSATURATION OF BUTADIENE RUBBERS I*

A. A. VASIL'EV

ALL-UNION RED BANNER OF LABOR S. V. LEBDEV SCIENTIFIC RESEARCH INSTITUTE

The unsaturation of rubbers is most frequently determined by utilizing their reaction with halogens. Other methods, for example, those based on reactions with dithiocyanogen[1] and with nitrobenzene[2], and methods based on oxidation[3], are not always reliable, or else are less convenient.

Kemp's method, which is usually employed to determine the unsaturation of natural rubber, is based on the use of iodine chloride dissolved in glacial acetic acid[4]. According to Kemp's data, solutions of bromine or of iodine bromide are unsuitable for this purpose, since the reaction with bromine is accompanied by intensive substitution, while the reaction with iodine bromide proceeds but slowly and does not reach completion[5]. More successful use of iodine bromide, under somewhat modified conditions, was made by Gorgas in his investigation of crude rubber[6].

Pummerer likewise used iodine chloride for the quantitative determination of double bonds in the natural rubber molecule[7]. Pummerer's method makes it possible to obtain a quantitative estimate of the substitution reaction, and this is its advantage, whereas it is inferior to Kemp's method in other respects.

The unsaturation of synthetic rubbers was determined by Cheyney and Kelley[8]. Using Kemp's method, these authors established that the reaction proceeds considerably more slowly with synthetic than with natural rubbers, and that the iodine numbers obtained are lower than those theoretically calculated (about 85–90 per cent). This fact is explained by the authors as due to the presence of connecting bridges between the molecules of these rubbers (butadiene and butadiene-styrene copolymers), or else to cyclization (butadiene-acrylonitrile copolymers). Attempts to estimate the extent of substitution during these determinations were not crowned with success. Similar results are reported by Medvedchuk and his collaborators in the case of a sodium-butadiene polymer obtained by the rod method[9].

Subsequently, Kemp and Peters dissolved samples of synthetic rubbers in *p*-dichlorobenzene and obtained results which were closer to those theoretically calculated[10]. However, the high temperature employed by these authors in the preparation of their solutions, as well as the presence of substitution (which they did not determine quantitatively), make it necessary to approach these data with certain reservations.

Rehner tested various methods of determining unsaturation as applied to Butyl rubbers. The highest values were obtained by determining unsaturation with the aid of halogens, more specifically by the method of Kemp-Wijs[11]. In the author's opinion, this is due to the accompanying substitution reaction; however, he, too, failed to carry out a quantitative estimation of the extent of this reaction.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by Alexander Bogrow, Science Translation Service, Cambridge, Mass., from the *Zhurnal Obshchei Khimii* (*Journal of General Chemistry* (USSR)), Vol. 17, No. 5, pages 923–928 (1947).

In evaluating the data obtained, the substitution reaction is frequently of decisive significance; in the investigations enumerated above, however, adequate attention is not always devoted to this phenomenon; in fact, it is totally ignored by some of the authors mentioned.

The extent of the substitution reaction is usually estimated on the basis of the quantity of hydrogen halide formed. In many cases, however, such measurements do not reflect the true conditions, since the formation of hydrogen halide may be caused by reactions other than substitution. It is known that, under the conditions employed in the determination, hydrogen halide may also be obtained by cleavage, with renewed formation of the double bond, or else as a result of hydrolysis, or, finally, as a result of cyclization; the probability of such reactions has been discussed repeatedly by various authors[12]. There can be no doubt that, in such cases, a correction introduced on the basis of measurements of the acid formed necessarily leads to erroneous conclusions.

Since it is very difficult to establish the existence and extent of each of the possible side reactions separately, it follows that the very fact that hydrogen halide is formed must be considered as an undesirable phenomenon, which makes doubtful the reliability of the results obtained. On the other hand, the absence of hydrogen halide in the reaction products bears witness to the absence of side reactions, and can serve as a criterion of the correctness and reliability of the determination.

From this point of view, the methods of Pummerer and Kemp cannot be considered satisfactory, at least when applied to butadiene rubbers; the former fails because of the formation of hydrogen halide during the reaction, while the latter is unsatisfactory because of the impossibility of estimating the quantity of acid formed.

CHOICE OF CONDITIONS FOR DETERMINING UNSATURATION OF BUTADIENE RUBBERS.

As a result of the present investigation, it was established that the reaction between butadiene rubbers and iodine bromide is not accompanied by side reactions if carbon tetrachloride is employed as a solvent. From Table 1, which summarizes the results of some of the experiments, it is evident that no formation of hydrogen halide is observed, in spite of wide variations in the quantity of reagent and in the reaction time. The reaction is completed in the course of 30 minutes, the quantity of reagent necessary being no less than 250–300 per cent of that theoretically required.

The nature of the solvent exerts a substantial effect on the development of side reactions. On substituting chloroform for carbon tetrachloride, a certain quantity of hydrogen halide is detected in the reaction products; the quantity of acid increases considerably if dichloroethane is used, and increases still further if tetrachloroethane is used as a solvent. The latter, in contrast to the other solvents, readily dissolves the reaction product formed; but in all other cases, as soon as the rubber solution and the reagent solution are combined, there is observed the separation of a fluocculent precipitate, which, however, does not prevent the reaction from proceeding to completion.

The last experiments in Table 1 show that irradiation with sunlight and with ultraviolet light during the reaction did not result in an increase of the quantity of halogen added, and that only a slight catalytic effect was produced by such treatment on the processes leading to the liberation of hydrogen halide. In this connection, it is interesting to note that, whereas in the former case,

TABLE 1

EFFECT OF VARYING REACTION CONDITIONS ON THE RESULTS OF UNSATURATION DETERMINATIONS

Rubber (type)	Conditions: Solvent	Conditions: Quantity of reagent (% of theory)	Conditions: Reaction (time)	Unsaturation (in %): Corrected for hydrogen halide*	Unsaturation (in %): Uncorrected for hydrogen halide
SKB-M	CCl_4	155	30 min.	—	75.1
	CCl_4	270	30 min.	—	86.4
	CCl_4	1450	30 min.	—	86.6
	CCl_4	320	3 hrs.	—	86.6
Rod polymerized sodium-butadiene	CCl_4	300	30 min.	—	87.0
	$C_2H_2Cl_4$	280	30 min.	52.5	88.3
	$C_2H_4Cl_2$	270	30 min.	64.7	88.5
	$CHCl_3$	290	30 min.	86.6	88.3
Rodless sodium-butadiene	CCl_4	270	30 min.	—	85.1
	CCl_4	260	3 hrs.**	85.7	87.8
	CCl_4	250	30 min.***	80.8	84.5

* A dash (—) indicates that no hydrogen halide was detected in these experiments.
** Reaction conducted in sunlight.
*** Reaction conducted under ultraviolet radiation.

i.e., during irradiation with sunlight, the formation of acid was brought about mainly by a substitution reaction, it would appear that no substitution reaction at all occurred in the case of irradiation with ultraviolet light, in spite of the presence of appreciable quantities of hydrogen halide.

As for the data obtained in experiments conducted with different solvents (dichloroethane and tetrachloroethane), they make it possible to conclude that, in these cases, the formation of acid resulted from the simultaneous occurrence of several side reactions, including substitution reactions.

These examples emphasize once more that only the absence of hydrogen halide in the reaction products can give assurance of reliability of the results obtained.

DETERMINATION OF UNSATURATION OF VARIOUS SYNTHETIC RUBBERS

Table 2 presents unsaturation values obtained with the aid of iodine bromide for various butadiene and synthetic isoprene rubbers, as well as for natural rubber and for some samples of Butyl rubber.

All samples of butadiene rubbers tested had an unsaturation ranging from 82 to 90 per cent on that theoretically calculated; thus, the method of preparation of these rubbers has no appreciable effect on their unsaturation.

The unsaturation values obtained for synthetic isoprene rubbers run higher than 100 per cent (102–107 per cent); those obtained for natural rubbers coincide rather closely with the calculated values (97.8–99.5 per cent) if no account is taken of the hydrogen halide formed. The reaction between isoprene rubbers and iodine bromide is always accompanied by the evolution of hydrogen halide; consequently the present method is inconvenient for operation with these rubbers. The reaction with iodine bromide can be employed also to determine the unsaturation of Butyl rubbers. In this case, too, in spite of the presence of only insignificant admixtures of isoprene links (in the isobutylene-isoprene polymer), the formation of hydrogen halide was observed.

TABLE 2

RESULTS OF UNSATURATION DETERMINATIONS FOR VARIOUS RUBBERS *

Rubber type	Unsaturation (in %)	
	Corrected for hydrogen halide	Uncorrected for hydrogen halide
From butadiene		
Rod-polymerized sodium-butadiene	—	87.0
Rod-polymerized potassium-butadiene	—	87.9
SKB-Ms	—	90.4
Rodless sodium-butadiene	—	85.1
SKB-M	—	86.4
Emulsion-polymerized DAB-II	—	82.3
Emulsion-polymerized G-54	—	87.6
Emulsion-polymerized with hydroperoxide	—	88.5
Obtained by homogeneous polymerization	—	89.1
From isoprene		
Rod-polymerized sodium-isoprene	70.8	102.4
SKB-IM	85.5	104.5
Emulsion-polymerized	88.5	106.9
Natural		
Pale crepe	78.5	99.5
Smoked sheet	86.3	97.8
Butyl rubbers		
Isobutylene-isoprene	0.2	1.2
Isobutylene-piperylene	—	2.0
Isobutylene-butadiene	—	2.2
Polyisobutylene, Vistanex, and Oppanol	—	0

* The data cited are confirmed by check determinations.

The property of rubbers containing isoprene links of producing hydrogen halide under the conditions indicated above, is a characteristic peculiarity of such rubbers, and can be utilized as a qualitative test to distinguish between butadiene and isoprene rubbers, as well as to indicate the presence of isoprene links in mixed polymers.

Table 3 shows the reproducibility of the results obtained in determining unsaturation in different samples of one and the same type of rubber.

Samples of rubbers prepared by one and the same method differ but little in their unsaturation. As for the spread between check determinations with one and the same sample, it does not exceed 1 per cent (absolute).

TABLE 3

REPRODUCIBILITY OF RESULTS OF DETERMINATION

Rubber type	Rod-polymerized sodium-butadiene		Rodless sodium-butadiene		SKB-M	
Sample no.	1	2	1	2	1	2
Iodine number:						
First determination	395	409	397	396	415	406
Second determination	390	—	400	400	412.0	404
Unsaturation (in %):						
First determination	84.0	87.0	84.5	84.2	88.3	86.4
Second determination	83.0	—	85.1	85.1	87.7	86.0

EXPERIMENTAL PART

The iodine bromide solution (Hanus solution) was prepared by dissolving 13 grams of sublimed iodine in one liter of dry pure carbon tetrachloride; thereupon, an equivalent quantity of purified bromine was added to the iodine solution. If the solution is prepared correctly, the titer of the iodine bromide solution is somewhat smaller than twice the titer of the original iodine solution[13]; otherwise, the excess of bromine may cause the occurrence of undesirable side reactions. The solution was stored in a drak bottle provided with a ground-glass stopper; no changes in the titer of the solution were detected in one month.

The reaction was carried out in a ground-glass stoppered 500-cc. Erlenmeyer flask; the ground-glass stopper was sealed to a glass stopcock, which, in turn, was connected to a 50-cc. thistle tube. The determination was carried out with a rubber sample weighing about 0.1 gram.

In view of the heterogeneity of rubbers frequently encountered, the correct selection of so small a sample involves certain difficulties, and may affect the precision of the determination; for this reason, there was prepared, to start with, a solution containing about 1 gram of rubber (weighed with a precision of ± 0.0001 gram) in 100 cc. of carbon tetrachloride. Ten cc. of this solution were measured out, and the precise weight of the sample used for the determination was established by weighing both portions of the solution. The smaller portion was then diluted with 30 cc. of carbon tetrachloride, and 50 cc. of the iodine bromide solution were added (from a burette); this constitutes about 270 per cent of the theoretically required quantity for butadiene rubbers, or about 340 per cent for isoprene rubbers. This operation was accompanied by the immediate precipitation of the reaction product.

The ground-glass joint of the flask was moistened with 2 or 3 drops of potassium iodide solution (to prevent losses), and the closed flask was allowed to stand in darkness, at room temperature, for a period of 30 minutes. Thereupon, 100 cc. of distilled water was added (a part of this quantity was first sucked in through the thistle tube while the flask was cooled with ice water); this was followed by 30 cc. of 10 per cent potassium iodide solution; and the content of the flask was rapidly titrated with a decinormal solution of sodium thiosulfate, and 5 cc. of a 5 per cent starch solution was added toward the end of the titration. During titration, especially toward the end, the flask must be very vigorously shaken after being closed with a cork. To destroy the emulsion which may be formed during this operation, it is useful to add 20–25 cc. of alcohol, as recommended by Pummerer.

Upon completion of the titration, 4 cc. of a 4 per cent solution of potassium iodate was added. If this resulted in the reappearance of a blue color, the titration was resumed and continued until the solution became colorless; if, on the other hand, no color appeared, this served to indicate the absence of hydrogen halide.

The quantity of halogen taking part in the reaction was determined by comparison with a control experiment, which was carried out under the same conditions, using the same quantities of solvent and reagent.

The unsaturation was calculated as the percentage ratio of the experimentally determined iodine number to the theoretically calculated value. In this connection, the theoretical iodine number for butadiene rubbers may be rounded off to 470, and that for isoprene rubbers to 373. This simplification exerts no substantial effect on the results of the calculation, and the resulting error does not exceed the limits of precision of the method.

In calculating the unsaturation values "corrected for hydrogen halide", the quantity of added halogen was determined by subtracting from the total quantity of halogen consumed twice the quantity of halogen detected in the form of acid. Such a calculation rests on a nominal basis, since, in this manner, all the acid that is found is assumed to have been formed by a substitution reaction, which, as already mentioned, does not always correspond to reality.

To determine the unsaturation of Butyl rubbers, the weight of the sample may be increased to 0.5 gram, and the reaction time may be reduced to 15 minutes; in this connection, the quantity of reagent must be no less than ten times theoretical. The unsaturation of Butyl rubbers was expressed as the percentage ratio of the experimentally determined iodine number to the iodine number of natural rubber.

The rubber samples employed in the investigation were prepared both under laboratory conditions and in pilot-plant units, as well as in full-scale plant equipment (production batches). For making available some of the samples, the author would like to express his gratitude to the following scientific workers of the All-Union Scientific Research Institute of Synthetic Rubber: M. A. Krupyshev, I. V. Rokityanskii, B. A. Matusov, and I. A. Livshits.

CONCLUSIONS

1. The reaction with iodine bromide in carbon tetrachloride solution represents a convenient method for determining the unsaturation of butadiene rubbers. The advantage of this method lies in the fact that the addition reaction is not accompanied by side reactions. This fact is confirmed by the absence of hydrogen halide, which can easily be determined by the usual methods, from the reaction products.

2. In contrast to butadiene rubbers, natural and synthetic isoprene rubbers produce copious quantities of hydrogen halide when allowed to react with iodine bromide under the same conditions. This property of natural and synthetic isoprene rubbers is a characteristic peculiarity of these rubbers and can be utilized for the qualitative detection of isoprene links in polymers under investigation.

3. The unsaturation of butadiene rubbers, as determined with the aid of the reaction with iodine bromide, is 85–90 per cent of the theoretically calculated value. The method by which these rubbers have been produced exerts no material effect on their unsaturation.

REFERENCES

[1] Pummerer and Stärk, *Ber.* **64**, 825 (1931); Medvedchuk, Aldoshin, Marovich, and Repman, *J. Gen. Chem.* (USSR) **12**, 220 (1942); Rehner, *Ind. Eng. Chem.* **36**, 118 (1944).
[2] Rehner, *Ind. Eng. Chem.* **36**, 118 (1944).
[3] Burger, Donaldson and Baty, ASTM Bull. No. **120**, p. 23 (1943); RUBBER CHEM. TECH. **16**, 660 (1943); Rehner, *Ind. Eng. Chem.* **36**, 118 (1944); Rehner and Gray, *Ind. Eng. Chem. Anal. Ed.* **17**, 367 (1945).
[4] Kemp and Mueller, *Ind. Eng. Chem. Anal. Ed.* **6**, 52 (1934).
[5] Kemp, *Ind. Eng. Chem.* **19**, 531 (1927).
[6] Gorgas, *Kautschuk* **4**, 253 (1928).
[7] Pummerer and Mann, *Ber.* **62**, 2636 (1929); Pummerer and Stärk, *Ber.* **67**, 292 (1934).
[8] Cheyney and Kelley, *Ind. Eng. Chem.* **34**, 1323 (1942).
[9] Medvedchuk, Aldoshin, Marovich, and Repman, *J. Gen. Chem.* (USSR) **12**, 220 (1942).
[10] Kemp and Peters, *Ind. Eng. Chem. Anal. Ed.* **15**, 453 (1943).
[11] Rehner, *Ind. Eng. Chem.* **36**, 118 (1944); Rehner and Gray, *Ind. Eng. Chem. Anal. Ed.* **17**, 367 (1945).
[12] Pummerer and Mann, *Ber.* **62**, 2636 (1929); Kemp and Mueller, *Ind. Eng. Chem. Anal. Ed.* **6**, 52 (1934); Rossmann, *Angew. Chem.* **48**, 223 (1935).
[13] Zinov'ev, "Chemistry of Fats", 1939, p. 229.

II

It is well known that, in a number of cases, the rate and completeness of a reaction with halogens is a function of the structure of the unsaturated organic compound. Whereas, with some of the latter, the reaction proceeds rapidly and quantitatively, others add the necessary quantity of halogen only with great difficulty, and sometimes the reaction does not reach completion at all, but stops at one or another level of saturation; in this connection, it frequently happens that different methods of determination lead to different results.

Difficulties arise most frequently in the presence of a conjugated system of double bonds.

TABLE 1

DETERMINATION OF UNSATURATION OF SOME HYDROCARBONS WITH THE AID OF IODINE BROMIDE

Name of hydrocarbon	Quantity of reagent (% of theory)	Reaction time	Unsaturation (in %)	
			Corrected for hydrogen halide*	Uncorrected for hydrogen halide*
Isobutylene	155	30 min.	—	99.5
Styrene	215	30 min.	—	100.8
Butadiene dimer (ethenyl-1-cyclohexene-3)	255	30 min.	—	97.9
Dicyclopentadiene	160	30 min.	43.1	79.2
	225	30 min.	49.9	110.1
Alloocimene (2,6-dimethyl-octatriene-2,4,6)	225	30 min.	74.1	82.1
	500	24 hrs.	67.3	100.5
Isoprene	150	30 min.	—	50.0
	300	30 min.	—	49.7
	800	168 hrs.	—	91.4
	690	15 days	—	95.3
Butadiene	145	30 min.	—	50.0
	665	30 min.	—	47.3
	655	240 hrs.	—	88.8
	675	15 days	—	101.9

* A dash (—) in this column (as well as in the corresponding columns of the subsequent tables) indicates that no hydrogen halide was detected in the reaction products.

Some compounds which are difficult to halogenate can still be fully saturated if a large excess of reagent is employed or if the reaction time is lengthened. For such substances, it is recommended to employ special methods of determination, most of which are suitable only for the given substance or group of substances, and which represent various modifications of the methods of Wijs, Hanus, or McIlhenny. In this connection, there have also been proposed such terms as "diene number", "apparent" iodine number, "long and rapid" iodine number, "total and partial" iodine number, etc.[1].

Table 1 presents data which illustrate the above-mentioned facts as exemplified by the reaction between some hydrocarbons and iodine bromide.

In the case of isobutylene, styrene, and butadiene dimer, the addition reaction proceeds smoothly and quantitatively. In the case of dicyclopentadiene and alloocimene, the reaction is accompanied by side-reactions and by the

evolution of considerable quantities of hydrogen halide; it is evident that, in this case, it is very difficult to estimate the quantity of halogen added. Finally, in the case of butadiene and isoprene, the reaction under the usual conditions stops after the fixation of only one of the double bonds; as for the subsequent addition of halogen, it takes place with great difficulty and only in the presence of a large excess of reagent and if the reaction time is prolonged to an extreme extent.

It was shown in the preceding communication[2] that a convenient method for determining the unsaturation of butadiene rubbers is offered by the reaction with iodine bromide in carbon tetrachloride solution. With the aid of this method, it was found that the unsaturation of butadiene rubbers, unlike that of natural and synthetic isoprene rubbers, is considerably lower than the theoretically calculated value and constitutes about 85–90 per cent of the latter.

TABLE 2

EFFECT OF VERY PROLONGED REACTION WITH IODINE BROMIDE ON RESULTS OF UNSATURATION DETERMINATIONS OF RUBBERS

Type of rubber	Quantity of reagent (% of theory)	Reaction time	Unsaturation (in %)	
			Corrected for hydrogen halide	Uncorrected for hydrogen halide
Rodless sodium-butadiene	770	7 days	—	95.7
	710	10 days	—	103.2
	710	15 days	112.4	115.1
	710	25 days	—	111.1
Rod-polymerized sodium-butadiene	270	8 days	90.4	98.7
	295	25 days	90.4	103.2
SKB-M	250	8 days	—	100.6
	270	25 days	106.2	107.4
	840	25 days	—	126.8
SKB-IM (Isoprene)	670	25 days	72.6	266.5
Pale crepe	660	25 days	36.8	221.5

It is possible to make two assumptions to explain this circumstance. On the one hand, the missing double bonds may, in fact, be absent, having been consumed to interlink the molecules (bridges) or to produce cyclization; on the other hand, this low degree of unsaturation may be merely apparent, being brought about by the presence of double bonds which are difficult to halogenate, as, for example, in compounds containing a conjugated system of double bonds. In the latter case, it would be possible to suppose that various modifications of the reaction conditions or the employment of other methods of determination might lead to other results, and these might be in better agreement with theory.

It was determined previously that, during the reaction with iodine bromide, the use of a large excess of reagent, the lengthening of the reaction time (to as much as three hours), and the use of different solvents, as well as the action of sunlight and ultraviolet rays, do not increase the quantity of halogen added. As concerns the reaction temperature, its rise stimulates the substitution reaction; but if kept within a narrow range (up to 35° C), this factor, as has been shown by experiments, exerts no appreciable effect on the results of the determination.

For this reason, it was only of interest to establish the influence of very prolonged reaction times (extending to several days), which are recommended in some cases for substances which are very difficult to halogenate.

As is seen from the data presented in Table 2, when the reaction time is very greatly prolonged (to as much as 7–25 days), the quantity of halogen taking part in the reaction increases considerably until, toward the end, the unsaturation values exceed the theoretically calculated values by substantial margins. It is possible that such excessive addition of halogen may be brought about by an actual rupture of the rubber molecules themselves.

The results obtained possess great interest[3]; on the other hand, they do not answer the question as to the presence in butadiene rubbers of double bonds which are difficult to halogenate or of conjugated double bonds, although these possibilities are not contradicted by these results. Moreover, these results show that great caution must be used in evaluating methods for determining unsaturation which propose the employment of long periods of time for the reaction between the halogen and the substance subjected to test.

COMPARATIVE DETERMINATIONS OF UNSATURATION IN RUBBER WITH THE AID OF REACTIONS WITH PYRIDINE SULFATE DIBROMIDE AND WITH IODINE CHLORIDE

The unsaturation values for butadiene rubbers obtained previously by the iodine bromide method were checked with the aid of the reactions with pyridine sulfate dibromide and with iodine chloride.

The pyridine method requires the use of glacial acetic acid for dissolving the reagent, and is consequently affected by the same defect as the method proposed by Kemp and Mueller[4], namely, by the difficulty of estimating the extent of side reactions. Nevertheless, the results obtained by this method are in close agreement with the previously cited values for the unsaturation of butadiene rubbers[2] (Table 3). This numerical order is also confirmed by data obtained with the aid of the iodine chloride reaction, on which the method of

TABLE 3

COMPARISON OF DIFFERENT METHODS FOR DETERMINING THE UNSATURATION OF RUBBER

	Unsaturation (in %)				
	Using BrI solution			Using ClI solution	
Type of rubber	Corrected for hydrogen halide	Uncorrected for hydrogen halide	Using $PyBr_2$ solution*	Corrected for hydrogen halide	Uncorrected for hydrogen halide
Rod polymerized sodium-butadiene	—	83.0	83.4	—	—
	—	84.0	84.2	—	—
Rodless sodium-butadiene	—	84.2		—	86.4
	—	85.1		—	86.8
SKB-M	—	88.3	89.8	—	—
	—	87.7	89.4	—	—
Rod-polymerized potassium-butadiene	—	87.9			
	—	89.4		88.5	91.7
SKB-IM (isoprene)	85.5	104.5		92.5	104.8
Pale crepe	78.5	99.5	101.0	—	97.8
Smoked sheet	86.3	97.8	101.0		

* The formation of hydrogen halide was not checked.

Pummerer[5] is based. However, in operating according to this method, the formation of small quantities of hydrogen halide was observed in some cases. This phenomenon is apparently unconnected with the nature of the rubber monomer, but is caused by certain other factors which it has not been possible to define up to the present time. It appears most probable that the phenomenon may be explained by the influence of the solvent employed, which, in this case, is chloroform.

It is also evident from the data in Table 3 that the pyridine sulfate dibromide method, after undergoing certain refinements, may be fully applicable to the determination of unsaturation in natural rubbers; it possesses a number of advantages over the method proposed by Kemp.

CHANGES IN UNSATURATION OF RUBBERS UNDER THE INFLUENCE OF VARIOUS FACTORS

Subsequently, the influence of various factors on the unsaturation of rubbers was investigated, both for the purpose of studying the causes of the lowered unsaturation of butadiene rubbers and to check the possibility of estimating these changes directly by the reaction with iodine bromide.

TABLE 4

CHANGES IN RUBBER UNSATURATION UNDER THE INFLUENCE OF VARIOUS FACTORS

Rubber (type)	Character of preliminary rubber treatment (in CCl_4 solution)	Unsaturation (in %) Corrected for hydrogen halide	Unsaturation (in %) Uncorrected
Rod-polymerized sodium-butadiene	Before treatment	—	87.0
	Sunlight for 8 days	—	77.8
Rodless sodium-butadiene	Before treatment	—	85.1
	Sunlight for 8 days	—	64.2
	UV rays for 45 min.	56.8	66.6
	80° C for 3 hrs. (in darkness)	—	83.6
Same, unmilled, no antioxidant added	Before treatment	—	86.8
	Sunlight for 18 days	—	84.0
	Sunlight for 46 days	—	50.6
	75° C for 4 hrs. (in darkness)	—	50.5
	Oxygen through solution for 1.5 hrs.	—	86.4
	Before treatment	78.5	99.5
	Sunlight for 8 days	78.0	87.6
	UV rays for 30 min.	9.7	92.2
	75° C for 4 hrs. (in darkness)	80.2	97.1

In view of the fact that most of the preparations go into solution only with difficulty or only partially following the various treatments to which they were subjected, these treatments were applied to rubber solutions in carbon tetrachloride. No visible changes in the solutions were observed as a result of these treatments, with the exception of slight yellowing in the case of some of the experiments; moreover, after prolonged irradiation (60 minutes and more) with ultraviolet rays, it was possible to observe the separation of polymer in the form of a thin film. The results of some of these experiments are presented in Table 4.

The heating of rubbers in solution at 75–80° C for three and four hours produces only slight changes in their degree of unsaturation. On the other

hand, after irradiation with sunlight for a period of eight days, the unsaturation is found to be greatly diminished, but in different degrees for the different rubbers. Roughly the same effect, but within a much shorter time (45 minutes), is attained by irradiating the rubber solutions with ultraviolet rays.

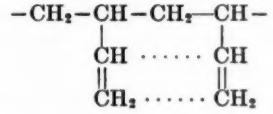
Milling (and the addition of antioxidant) has almost no effect on the unsaturation of butadiene rubber. (This has also been noted with respect to natural rubber[6].)

Compared with the solution of milled rubber, the solution of unmilled rubber shows considerably higher stability with respect to the action of sunlight. On the other hand, on treatment with gaseous oxygen, no changes whatever in unsaturation could be observed. Apparently the quantity of oxygen added during this process is so small that the sensitivity of the method is insufficient to reflect the resulting change in unsaturation.

Thus, the present investigation shows that, during the reaction between butadiene rubbers and halogens, it is impossible to attain saturation higher than 85–90 per cent of the theoretical values.

The supposition voiced by Cheyney and Kelley[7], that this circumstance is explained by the presence of intermolecular cross-linking and by cyclization, can scarcely be considered as providing the only possible reason for the lowered degree of unsaturation. The expenditure of so considerable a number of double bonds to produce interlinkages would have to be strongly reflected in the properties of these rubbers, bringing their properties close to those of vulcanized rubbers; such rubbers, therefore, would hardly be suitable for the manufacture of rubber products.

It may be assumed that, along with the existence of intermolecular cross-linkages, a certain part of the double bonds is expended on intramolecular cyclization; for example, between the two neighboring vinyl groups of butadiene molecules which are connected at the 1,2-position:



The existence of such intramolecular cycles is very probable since it must be reflected to a considerably smaller degree in the properties of a rubber than the presence of intermolecular cycles and bridges. Moreover, it must also be kept in view that the lowered unsaturation may likewise be produced in part by the presence in the molecules of these rubbers of double bonds resistant to halogenation or of conjugated systems of double bonds. However, it appears to be impossible to verify these suppositions experimentally with the aid of a reaction with halogens.

EXPERIMENTAL PART

The determination of unsaturation by the iodine bromide method was described in the preceding communication[2].

In the investigation of hydrocarbons (monomers), carbon tetrachloride was used as the solvent. The weighed samples of low-boiling hydrocarbons (isobutylene, butadiene, and isoprene) were confined in ampoules; the samples were cooled at the beginning of the reaction, and then the temperature was gradually increased until room temperature was attained.

The solution of pyridine sulfate dibromide was prepared by the method of Rosemund and Kuhnhenn[8]. For convenience in operation, a double-strength solution was prepared; it is possible that this circumstance partially explained

the extreme instability of the reagent, whose titer already changed within the first few days. In this connection, along with carbon tetrachloride, chloroform can also be used for dissolving the rubber. Preliminary experiments showed that 30 minutes are enough to complete the reaction, and that the quantity of reagent must constitute about 200–240 per cent of that theoretically required; the reaction with natural rubber proceeds considerably more rapidly, and is completed within three to five minutes. As already mentioned, the presence of glacial acetic acid in the capacity of solvent for the reagent makes it impossible, in these determinations, to estimate the quantity of hydrogen halide formed.

The unsaturation determinations with the aid of iodine chloride were carried out in accordance with Pummerer's[5] directions. The reaction was conducted for six hours at room temperature (the results of the determination remaining unchanged by carrying out the reaction for 12 hours at 0° C). The quantity of reagent constituted about 120 per cent of that theoretically required; with a larger excess, increased formation of hydrogen halide was observed.

The rubber solutions used for evaluating the effects of sunlight and ultraviolet rays and for thermal treatments were prepared in a concentration of approximately 0.6 per cent (about one gram of rubber in 100 cc. of carbon tetrachloride). The results obtained in these experiments were compared with the data of control experiments, in which the solvent was treated in the same manner and under the same conditions. In the majority of cases, when such treated rubber samples were subsequently titrated with sodium thiosulfate, the formation of rather stable emulsions was observed; the addition of 20 cc. of alcohol before titration eliminated this phenomenon to a considerable extent.

CONCLUSIONS

1. The data on the unsaturation of butadiene rubbers previously obtained by using the method based on the reaction with iodine bromide have been checked and confirmed with the aid of the reactions with pyridine sulfate dibromide and with iodine chloride.

2. The influence of various factors on the unsaturation of butadiene rubbers has been checked, and the possibility of estimating changes in unsaturation with the aid of the reaction with iodine bromide has been established.

3. The present investigation shows that, during the reaction between butadiene rubbers and halogens, it is impossible to attain a degree of saturation exceeding 85–90 per cent of the theoretical values. This is apparently due to the existence of intramolecular cyclization, to the presence of intermolecular connecting bridges, and possibly to the presence of double bonds resistant to halogenation or of conjugated double bonds in the molecules of these rubbers.

The reaction with halogens offers no possibility of confirming these suppositions experimentally.

REFERENCES

[1] Rossmann, *Angew. Chem.* **50**, 187 (1937); Mikusch and Frazier, *Ind. Eng. Chem. Anal. Ed.* **13**, 782 (1941); **15**, 109 (1943).
[2] Vasil'ev, *J. Gen. Chem.* (USSR) **17**, 923 (1947).
[3] Rossmann (*Angew. Chem.* **50**, 187 (1937)) cites an analogous example in American tung oil. Instead of the addition of the calculated three molecules of bromine, he observed the addition of four molecules, and the reaction proceeded without evolution of hydrogen halide.
[4] Kemp and Mueller, *Ind. Eng. Chem. Anal. Ed.* **6**, 52 (1934).
[5] Pummerer and Stärk, *Ber.* **64**, 835 (1931).
[6] Kemp, *Ind. Eng. Chem.* **19**, 531 (1927).
[7] Cheyney and Kelley, *Ind. Eng. Chem.* **34**, 1323 (1942).
[8] Rosemund and Kuhnhenn, *Z. Nahr. u. Genussm.* **46**, 154 (1923); Golde, "Fats and Oils", **1933**, Vol. 2, p. 128.

THE ABNORMAL MELTING OF RAW RUBBER *

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INTRODUCTION

It is a well known fact that amorphous raw rubber exists in a supercooled metastable state, even at relatively low temperatures[1], and this fact has been explained by the present authors, using statistical mechanics[2]. But Bekkedahl and others[3] have found recently a very peculiar fact with respect to raw rubber in this state; that is, not only the time rate of crystallization but also the melting range is different according to the temperature at which crystallization occurs. They suggest that the reason why the melting points as previously determined by various investigators spread widely, and that the β-anomaly of Ruheman and Simon[4], and other queer phenomena may have their origin in this fact.

As this phenomenon is so strange, and it seems no explanation has been offered as yet, the authors wish to offer some interpretation in the next paragraph. In this paper we shall discuss only abnormal melting, because the main phenomena of crystallization of supercooled raw rubber seems to be the same as in other substances, even if they differ in details.

THE MELTING OF CRYSTALLIZED RAW RUBBER

A sample of raw rubber annealed at 55 C is brought quickly to a temperature of crystallization (in Figure 1, $-32°$, $-17°$, $1°$, $8°$, and $14°$ C) and crystallized; its specific volume decreases about 2 per cent. When the crystallization is completed, the temperature is raised at the rate of about 0.5° C per minute; then its specific volume increases first linearly along the straight line characteristic of the crystalline state[5] (Figure 1). At about 5 degrees above the crystallization temperature, it deviates suddenly upward from the straight line. Finally when it reaches the upper straight line characteristic of the amorphous state, melting comes to an end.

The points where melting starts and is completed are functions of the temperature of crystallization, and are independent of the degree of crystallization. This relation is shown[5] in Figure 2.

The cause of this phenomenon which is perceptible at once is the existence of many crystal grains in the crystalline state, whose size and melting points differ according to the temperature at which they were formed.

But this does not seem to be the case because when we cease to raise the temperature, recrystallization occurs. This shows that the true thermodynamical equilibrium state is not the partially melted state but the completely crystallized state. Moroever, the experiments of Ruheman and Simon[4] show that the β-anomaly, which is clearly associated with this abnormal melting as indicated by Wood[6], is not reproducible. The authors state: "In contrast to the α-anomaly, the β-anomaly was not strictly reproducible. Depending on

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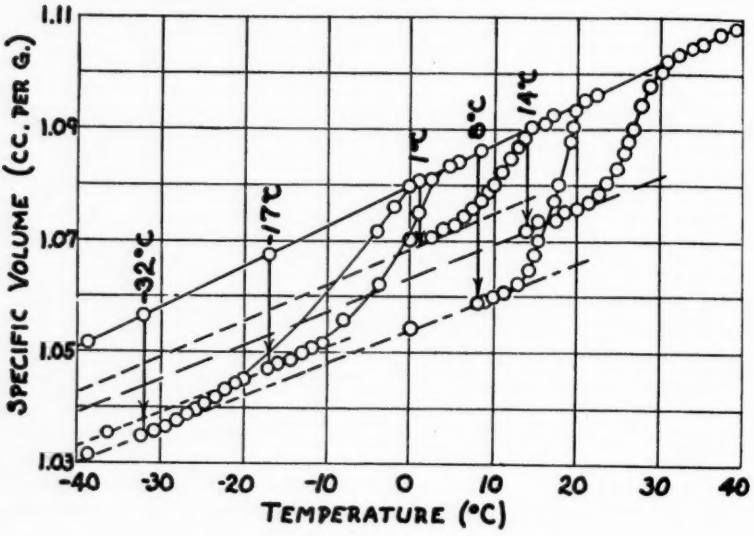

FIG. 1.—Melting of crystallized raw rubber.

the speed of heating as well as the previous cooling the curve is steeper or flatter. Also the energy, that is, the area under the curve, was different in different measurements." In this connection, it may be noticeable that the melting curves in Figure 1 do not resemble the typical S curve of crystallization (even if the abscissa is changed), and the melting points of paraffin homologs converge about 400° K at relatively low states of polymerization.

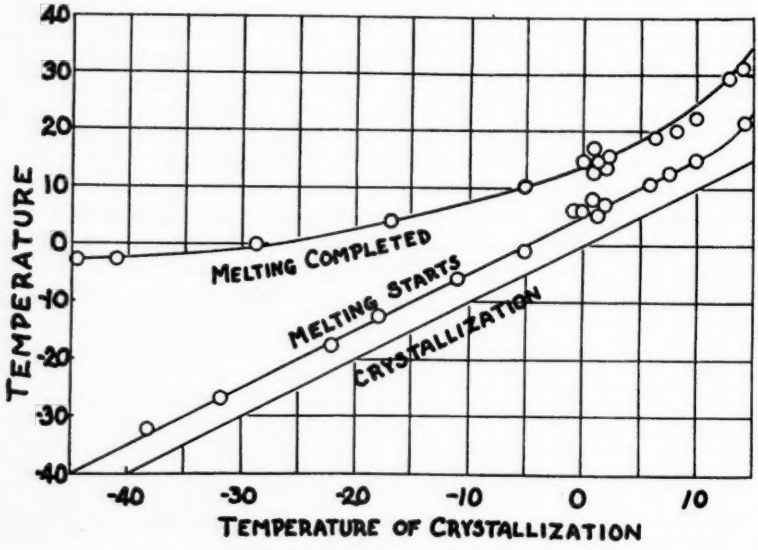

FIG. 2.—The melting range of crystallized raw rubber as a function of the temperature of crystallization.

THEORY OF ABNORMAL MELTING

The first problem concerning the melting phenomena is whether they are thermodynamical equilibrium phenomena or rate effects. Bekkedahl states: "It was found in preliminary experiments that, at a heating rate of 0.5° C per minute or less, no observable differences from the equilibrium values of the volume could be noted, and there was found to be no evidence of time lag or delay in melting of crystals after the establishment of thermal equilibrium. For example, at any constant temperature in the melting range, the volume was not observed to increase with time. In this range, if the temperature is lowered, the volume-temperature relation is observed to be linear and intermediate between the amorphous and crystalline volumes. Rubber in the partially melted state can, however, undergo additional crystallization, with a resulting decrease of volume."

We cannot deduce under what kind of conditions the preliminary experiment was performed, but it is understandable that the true thermodynamical equilibrium state is not in the partially melted state but in the crystalline state in this range. In the previous paper[1] the volume-temperature curve of the amorphous state deviates from the straight line at the heating rate of 0.02–0.03° per minute at about −25° C, and approaches that of the crystalline state. On the other hand, the experiments of Ruheman and Simon show the influence of heating rate as stated above. In the experiment of Bekkedahl and others, the heating rate seems to be about 0.5° per minute. (The whole time needed to cover the 10° C of melting range was about 20–30 minutes.)

But a high polymer shows relaxation in thermal expansion. For example, the relaxation time of polystyrene is about 5 minutes, and the approach to the equilibrium value is nearly exponential[7]. Accordingly the relaxation effect must be taken into consideration in the present problem.

Now amorphous particles or amorphous nuclei in crystalline particles may exist, for the kinetic units of crystallization and melting are not molecules themselves but "segments", and here we call them simply particles just as the crystalline nuclei in the amorphous particles, and the relaxation times of both states must be different; the former may be smaller, as its state resembles that of a gas.

Then if we raise the temperature at a suitable heating rate a, the amorphous particles denoted by A_1, A_2, in Figure 3 may expand more rapidly than the other crystalline parts C_1, C_2, C_3 and compress at that moment such parts as C_2 held between A_1 and A_2 and will "buckle" them, and consequently melting takes place. The force acting there is of course not isotropic pressure. If we keep the temperature constant at that point, this scheme of melting stops, and they fall into the equilibrium crystalline state. At first, melting may be very slow, as the amorphous particles in the crystalline state or the amorphous nuclei are very small in number, and therefore recrystallization is comparatively predominant over the expansion of volume. But it becomes more extensive according as the temperature rises and the number of amorphous particles as well as their mobility (in comparison with that of crystalline particles) increase. But when melting is nearly completed, the stress becomes very small again, as the outer surface is free, and the volume approaches asymptotically to that of the amorphous state.

To treat these phenomena quantitatively, we denote by v_0 the average volume of an amorphous nucleus at crystallization temperature T_c, and by α its thermal expansion coefficient. Then its equilibrium volume at temperature T

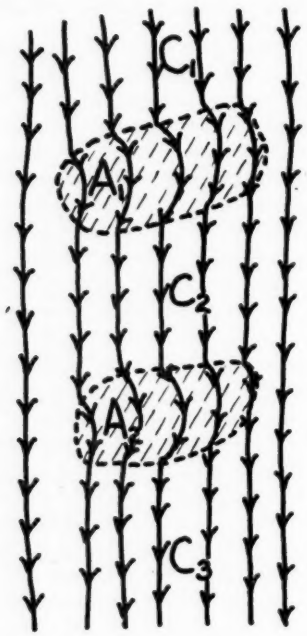

FIG. 3.—Schematic representation of amorphous nuclei in crystallized particles.

is given by $(1+\alpha(T-T_c))v_0$. But when we raise the temperature at a suitable heating rate, its volume does not reach this value when the temperature becomes T. We denote this actual volume by v. Thereafter it approaches the above equilibrium value with relaxation time λ nearly exponentially. Therefore, the volume-increase δv after the moment when the temperature reaches T is given by:

$$\{1 + \alpha(T - T_c)v_0 - v(T - T_0)\}\{1 - e^{-(\delta t/\lambda)}\} = \delta v \tag{1}$$

Here λ may be represented as follows:

$$\lambda = \lambda_0 e^{Ea/kT} \tag{2}$$

For convenience we denote:

$$\left.\begin{aligned} T - T_c &= \tau \\ a &= \frac{dT}{dt} \end{aligned}\right\} \tag{3}$$

Then the differential equation determining the volume-temperoture relation is (by expanding exp $(-(\delta t/\lambda))$):

$$\frac{dv}{d\tau} = \frac{1 + \alpha\tau}{a\lambda} v_0 - \frac{v}{a\lambda} \tag{4}$$

This equation resembles an ordinary relaxation equation, but not exactly, because in this case the final volume continuously changes with temperature or with time.

To integrate this equation we assume that the variation of λ with temperature is small compared with that of τ/a, and assume it constant for the moment.

Such an approximation may be sufficiently accurate at least when the temperature is high enough. As the heating rate is constant, we obtain:

$$v = v_0\{1 + \alpha\tau - \alpha a\lambda(1 - e^{-(\tau/a\lambda)})\} \tag{5}$$

The meaning of this equation is obvious.

Then we consider a hole in crystalline particles surrounding these amorphous volumes v as in Figure 4. It expands with relaxation time μ:

$$\mu = \mu_0 e^{E_c/kT} \tag{6}$$

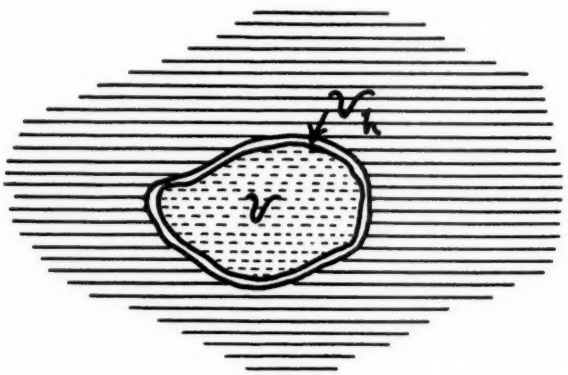

FIG. 4.—Amorphous nucleus and the surrounding crystalline hole. The volume of each state is designated by v and v_h, respectively.

The equilibrium volume of the hole is attained when its volume reaches that of the amorphous nucleus. Then we obtain, as in the case of Equation (4), the differential equation determining the volume of the hole:

$$\frac{dv_h}{d\tau} = \frac{1 + \alpha\tau}{a\mu} v_0 - \frac{v}{a\mu} \tag{7}$$

If the expansion of the hole is not rapid enough, it may be overcome by expansion of the amorphous particles. But in reality melting takes place before such events occur. This process of "invasion" by amorphous particles is perhaps a rapid reaction, and it reveals no time lag. We assume that the rate is proportional to the difference between the time rates of thermal expansions of two states, that is:

$$\frac{dn}{d\tau} = Kn\left\{\frac{dv}{dt} - \frac{dv_h}{dt}\right\} \tag{8}$$

where n is the total number of amorphous particles and K is a proportional constant. In this equation it is also assumed that melting becomes more effective as the amorphous particles increase. Then to the same approximation as in Equation (5), we obtain:

$$n = n_c \exp\left[K\left(1 - \frac{\lambda}{\mu}\right) v_0\{\tau - a\lambda(1 - e^{-(\tau/a\lambda)})\}\right] \tag{9}$$

Here n_c is the number of amorphous particles at T_c.

If $\lambda = \mu$ or $K = 0$, $n = n_c$ as naturally expected.

Particularly, if τ is small:

$$v = v_0 \left(1 + \frac{\alpha\tau^2}{2a\lambda} - \frac{\alpha\tau^3}{6(a\lambda)^2} + \cdots \right) \tag{10}$$

$$n = n_c \left\{ 1 + K \left(1 - \frac{\lambda}{\mu} \right) v_0 \left(\frac{\tau^2}{2a\lambda} - \frac{\tau^3}{6(a\lambda)^2} + \cdots \right) \right\} \tag{11}$$

The point T_i, where melting starts, can be obtained by equating the second derivative of the right hand member of Equation (11) to zero:

$$\tau_i = T_i - T_c = a\lambda \tag{12}$$

or

$$\frac{T_i - T_c}{a} = \lambda \tag{13}$$

That is, melting starts when the time interval of observation approaches the relaxation time λ. In this equation the temperature in the expression of λ must be taken to be the mean value of T_c and T_i, but the difference may be negligible, even if we take it for T_c. Then:

$$\log (T_i - T_c) = \log a\lambda_0 + \frac{E^a}{kT_c} \tag{14}$$

This relation is shown in Figure 5.

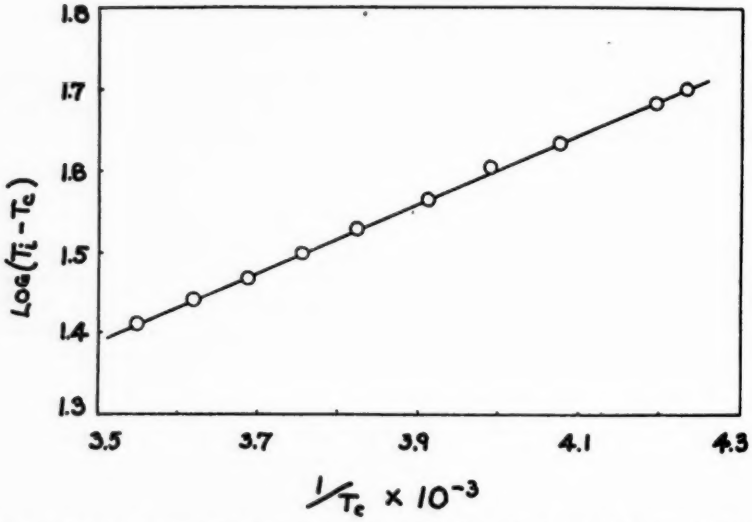

FIG. 5.—Relation between the temperature of crystallization and the point where melting starts. The circles show the experimental data from Figure 2.

From this figure we obtain:

$$a\lambda_0 = 5.3 \tag{15}$$

Accordingly if the heating rate a is 0.5° per minute,

$$\lambda_0 = 10.6 \text{ min.} \tag{16}$$

This value seems to be plausible. Also the activation energy E_a is found to be 4.4 k, but this value is not reliable, since it is assumed that the variation of λ with temperature is small.

It has been reported that the apparent second order transitions of polystyrene[7] and other high polymers occur when the time interval of observation becomes comparable to the relaxation time[8]. In this case only one state comes into question and only the relation (10) is necessary, and a conclusion analogous to the above statement can be deduced.

The point T_f where melting completes itself is determined by the condition that the number of amorphous particles becomes equal to N—the total number of particles. In this case the last term of Equation (9) can be neglected, and if we put:

$$A = K\left(1 - \frac{\lambda}{\mu}\right) v_0 \tag{17}$$

then the temperature is given by:

$$\begin{aligned} N &= n_c \exp\left[A(\tau_f - a\lambda)\right] \\ \tau_f &= T_f - T_c \end{aligned} \tag{18}$$

In these equations, v_0 is the volume at temperature T_c, but the error is negligible, even if it is independent of T_c.

To determine the explicit dependence of τ_f on T_c, we must determine n_c as a function of crystallization temperature. This dependence can be obtained as follows.

The amorphous particles or nuclei are oscillating with frequencies different from those of crystalline particles surrounding them. For simplicity we take the Einstein model for each state and designate the characteristic frequencies of the amorphous and crystalline state as ν', and ν, respectively. If we denote by W the work done to produce an amorphous particle in crystalline state, then the partition function Z of the whole system can be written as follows:

$$Z = e^{-(nW/kT)} \frac{1}{(1 - e^{-(h\nu/kT)})^{3(N-n)}} \frac{1}{(1 - e^{-(h\nu'/kT)})^{3n}} \frac{N!}{n!(N-n)!} \tag{19}$$

From this we can determine the equilibrium value of n as a function of temperature by minimizing the free energy calculated from the above equation. If the temperature is high we can thus obtain approximately:

$$\frac{n}{N} = \gamma e^{-(W/kT)} \tag{20}$$

where

$$\gamma = \nu/\nu'$$

The amorphous particles increase according to Equation (20) as the temperature rises. But when it is raised a definite rate, they do not immediately reach this value, especially in such substances as rubber. Because, for the occurrence of it, molecules must move as a whole, and this is particularly difficult in high polymers. Accordingly, we can express in this case Equation (20) as follows:

$$n = n_0 e^{-(W/kT_c)} \tag{21}$$

where n_0 is a constant independent of T_c.

From Equations (18) and (21) we obtain:

$$T_f = T_e + a\lambda + \frac{W}{AkT_e} + \frac{1}{A}\log\frac{N}{n_0} \qquad (22)$$

where A is a function of temperature according to Equation (17), but we can neglect this variation according to the above assumption. Therefore, $(T_f - T_e - a\lambda)$ *vs.* $1/T_e$ must be linear (Figure 6). This linearity is in accordance with experiment particularly at higher temperatures. The deviation at lower temperature is legitimate. As in this case the melting range is very wide (*cf.* Figure 2) and the variation of the relaxation time with temperature is great, the above assumption fails. Also the determination of the end point itself is rather difficult, owing to recrystallization, and the experimental error due to this fact may have some influence on the result. At any rate the theory is more accurate at higher temperatures, and the calculated melting curve is shown by the heavy curve in Figure 7 as an example. The calculated curve represents the experimental one fairly well, although this seems rather unimportant.

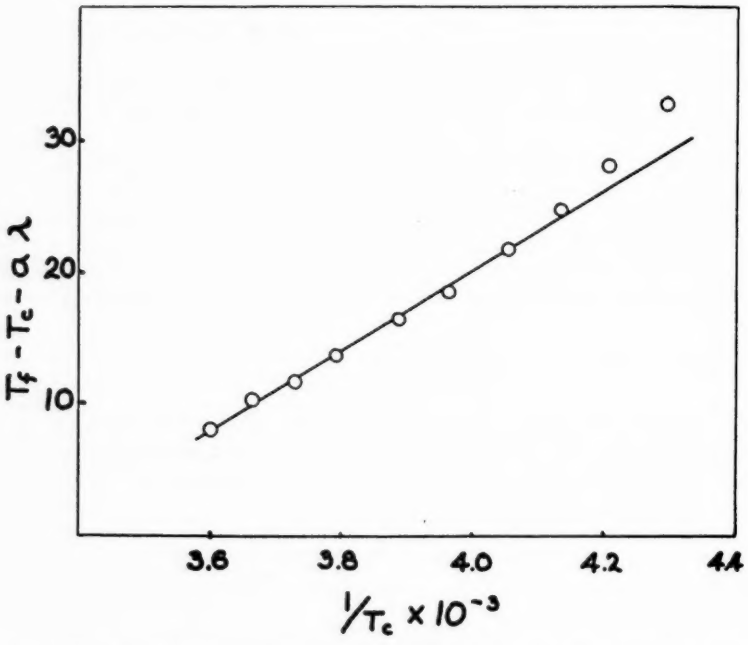

FIG. 6.—Relation between the crystallization temperature and the point where melting is complete. Circles show the experimental data from Figure 2.

It should be noted that we have determined the end point in a somewhat different way compared with the starting point. It was determined from Equation (21), and the temperature in this equation represents that which gives the equilibrium number of amorphous nuclei. If we crystallize a sample of amorphous rubber at some temperature or stop crystallization at an intermediate stage and bring it to another temperature and keep it there for a time interval

comparable to the time needed for the first crystallization, then the distribution of amorphous nuclei may be a function of both temperatures. In other words it has a hysteresis character. Also the starting point itself may become more complicated in such a treatment, because the deviation from the equilibrium value sets in when the time interval of observation becomes comparable to the relaxation time. However, there may be various kinds of relaxation time in the case of such a treatment, and "stark rubber" may be such a case.

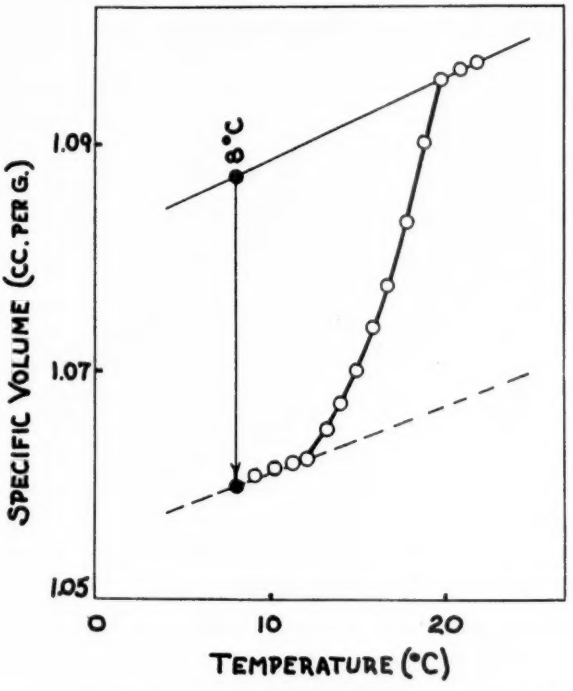

FIG. 7.—Melting curve of the sample crystallized at 8° C. The heavy curve is the theoretical.

As the last explanation shows, the end point is not merely the point where the time interval of observation becomes comparable to the relaxation time of hole μ, but it is determined by this quantity at any rate, and the melting range itself seems to be the domain between the curve λ and μ—the shaded part in Figure 8. In the figure, the straight line passing through T_c represents the time of observation.

Attention should be drawn also to certain other facts. First, the right hand side of Equation (13) does not depend on the degree of crystallization, and this is also approximately true for the end-point, in accordance with the experimental result. Secondly, if we raise the heating rate, the starting point becomes higher and the melting curve itself becomes steeper. Thirdly, if these ideas are correct, these phenomena may be more pronounced in raw rubber than in vulcanized rubber, as the difference of the two relaxation times and the relaxation times themselves in the former may be greater than those in the latter. Finally, we should not neglect recrystallization, particularly when the

heating rate is very small. When we raise the temperature very slowly, the sample may expand merely with the expansion coefficient of crystalline state (the effect of amorphous nuclei is very small) and the "invasion" by amorphous nuclei does not appear. If the heating rate is very large and the crystalline sample is brought as it was to the range in which the state of amorphous rubber is more stable than the crystalline, *i.e.*, to the range above the "true melting point", the sample melts at this point, independently of its crystallization temperature. In other words, the phenomena discovered by Bekkedahl take place most strikingly at a suitable heating rate.

It is hoped that these conclusions will be put to experimental tests.

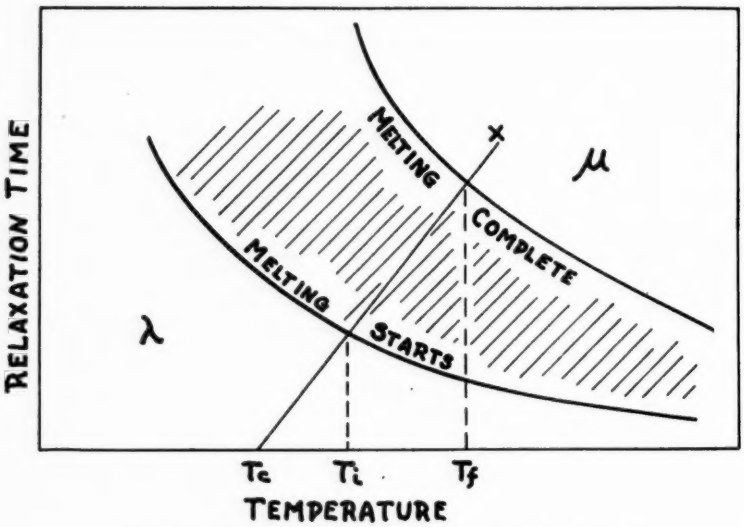

FIG. 8.—Physical meaning of the melting range shown in Figure 2.

ACKNOWLEDGMENT

In conclusion, we wish to express our hearty thanks to Professor T. Sakai for his kind guidance, and also to T. Saito, R. Kikuchi and K. Ichimura for their valuable discussion of the present subject.

SUMMARY

The experimental results on the abnormal melting of crystallized raw rubber by Wood and Bekkedahl are studied theoretically. The effect can be explained by the fact that the relaxation time for the thermal expansion of crystalline particles differs from that of amorphous particles. At the point where the melting begins, the time interval of observation becomes comparable to the relaxation time of amorphous particles. The point becomes higher as the time rate of heating increases, and also as the relaxation time itself becomes larger. The point at which fusion is complete is determined by the relaxation times of the amorphous and crystallized states, heating rate, and previous history. This effect becomes large at a suitable heating rate, and is larger in natural rubber than in vulcanized rubber.

REFERENCES

1 Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934); **15**, 503 (1935).
2 Sakai and Isihara, *Ōyobuturi* **15** (Showa 21), 1.
3 Bekkedahl and Wood, *J. Chem. Physics* **9**, 193 (1941); Wood and Bekkedahl, *J. Applied Physics* **17**, 362 (1946).
4 Ruhemann and Simon, *Z. physik. Chem.* **A138**, 1 (1928).
5 Wood and Bekkedahl, *J. Applied Physics* **17**, 362 (1946).
6 Wood, *J. Chem. Physics* **10**, 403 (1942).
7 Spencer and Boyer, *J. Applied Physics* **17**, 398 (1946).
8 Alfrey, Goldfinger and Mark, *J. Applied Physics* **14**, 700 (1943); Boyer and Spencer, *J. Applied Physics* **15**, 398 (1944); **16**, 594 (1945).

STRUCTURAL CHANGES IN RUBBER BROUGHT ABOUT BY MOLECULAR OXYGEN. III. PROPERTIES OF DISINTEGRATED VULCANIZED NATURAL RUBBER*

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In the preceding communication[1], the process of dissolution of vulcanized rubber on heating it in hydrocarbon media in the presence of molecular oxygen was described. This process was considered to be a result of oxidation and disintegration of molecular chains in the spatial structure of the vulcanizate; in other words, it was interpreted by us as a process of destructive solution. The properties of disintegrated vulcanized rubber are described below, with particular reference to the properties of the resulting solutions, which, in our opinion, represent a special class of colloidal systems.

1. CHEMICAL CHARACTERISTICS

The process of disintegration of a vulcanized rubber film in acid as previously described gives a light yellow opalescent solution. On standing, this solution precipitates a fine sediment, which consists mainly of zinc oxide originally in the vulcanizate. If the concentration of the supernatant clear solution is not less than 1.5 per cent, the action of acetone on it results in the separation of about 70 per cent of the substance in the form of a sticky mass, which, after being dried in vacuo at 20° C, is completely soluble in all ordinary rubber solvents. The combined sulfur content of the product separated by acetone constitutes 1.98 per cent, which corresponds precisely to the combined sulfur content of the original vulcanizate. The coincidence between the data which characterize the combined sulfur content in the original vulcanizate and in its disintegration products may serve as a direct indication of the fact that combined sulfur plays an essential part in the molecular structure of vulcanized rubber and is distributed in the latter with great uniformity.

The oxygen content of the disintegration product separated by acetone was determined by burning the product, mixed with carbon black, in a current of nitrogen[2]. It constitutes about 50 mg. per gram of substance. Of this quantity, 3.77 mg. falls to the share of oxygen contained in free carboxyl groups (the acid number of the dispersed product being 6.6). Thus, each carboxyl group in the disintegrated vulcanizate is associated with a hydrocarbon residue, the molecular weight of which is about 8000.

The presence of a large number of polar groups containing oxygen and the relatively low molecular weights of the disintegration products of the vulcanizate explain why, in addition to the usual rubber solvents, these products are fairly readily soluble in binary solvent media containing associated liquids (benzene-alcohol mixtures). The acetone extract of the vacuum-dried product constitutes 53 per cent.

* Translated for Rubber Chemistry and Technology by Alexander Bogrow, Science Translation Service, Cambridge, from the *Zhurnal Obshcheĭ Khimiĭ* (*Journal of General Chemistry*), Vol. 17, No. 12, pages 2222–2227 (1947).

2. VISCOSITY AND LIGHT DIFFUSION OF SOLUTIONS OF DISINTEGRATED VULCANIZED RUBBER

Viscosity was measured with the aid of a Scarp viscometer[3], with which it is possible to use insignificant quantities of the liquid being examined.

In contrast to unvulcanized rubber, the viscosity of disintegrated-vulcanizate solutions obeys a linear relationship (Figure 1) over a wide range of concentrations (up to 6 per cent), as indicated by the following equation:

$$\frac{\eta_{sp}}{vc} = k \tag{1}$$

where η_{sp} is the specific viscosity, v is the specific volume of the vulcanizate, and c is the concentration. The constant k is a function of the extent of disintegration of the vulcanizate. For an acetone-separated product in carbon tetrachloride, the mean value of the constant at 20° C equals 48. The theory of viscosity in dilute suspensions relates the value of the constant k to the asymmetry in the shape of particles in the dispersed phase. We made use of the equation of Simha[4], according to which:

$$k = \frac{(b/a)^2}{15[\log 2(b/a) - \frac{3}{2}]} - \frac{(b/a)^2}{5[\log 2(b/a) - \frac{1}{2}]} + \frac{14}{15} \tag{2}$$

where b/a is the ratio between the axes of the ellipsoid of rotation which characterizes the mean size of the particles. In our case, with the constant $k = 48$, this ratio equals 24. As calculated with the aid of the same formula by Pasynskiĭ and Gotovskaya[5], the ratio between the axes of the particles of a sol fraction of natural rubber is 117–123; according to the experiments of Novikov[6], who measured birefringence in a current of plasticized butadiene-styrene rubber, this ratio is approximately 100. The data cited above indicate that the particles of a disintegrated vulcanizate differ appreciably in their configuration from the linear molecules of unvulcanized rubber.

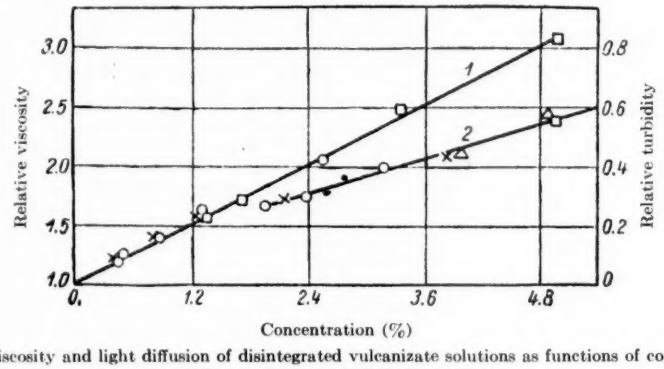

FIG. 1.—Viscosity and light diffusion of disintegrated vulcanizate solutions as functions of concentration. 1: Relative viscosity; 2: Relative turbidity.

The diffusion of light by disintegrated vulcanizate solutions in xylene was determined with the aid of a Leitz nephelometer in comparison with a standard turbid substance. As is evident from Figure 1, the intensity of light diffusion bears a linear relationship to the concentration, whereas the relationship is more complex for solutions of crude rubber. This indicates that the particles of dispersed vulcanizate are relatively large and relatively little solvated.

3. MOLECULAR WEIGHT AND MOLECULAR SHAPE OF DISINTEGRATED VULCANIZATE

The molecular weight of the disintegrated vulcanizate was determined with the aid of the equation of Polson[7], the applicability of which to the calculation of molecular weights of high-molecular compounds has been demonstrated in the researches of a number of investigators[5]. Polson's equation can be formulated as follows:

$$M = \frac{k}{D^3(f/f_0)^3 v} \tag{3}$$

where M is the molecular weight of the solute, D is its coefficient of diffusion, (f/f_0) is the asymmetry factor of the particles of the solution, and v is the specific volume. The constant k is expressed as follows:

$$k = \frac{(RT)^3}{162\pi^2\eta^3 N^2}$$

For carbon tetrachloride, which was employed by us as the solvent, k equals $2.70 \cdot 10^{-14}$ at 20° C. The asymmetry factor (f/f_0) is found with the aid of the Perrin-Hertzog equation[8] from the axial ratio previously determined by us from viscometric data, which characterizes the particles of disintegrated vulcanizate. In our case, $f/f_0 = 2.15$. The coefficient of diffusion was determined experimentally by the method of Lamm in an apparatus described in detail elsewhere[5]. The principle of Lamm's method consists in photographing a micrometric scale through a column of liquid in which the substance under investigation diffuses. Owing to the existence of a vertical gradient of concentration, there is a shift of the scale divisions, which is determined by comparison with a photograph through the pure solvent. This shift is proportional to the concentration gradient. To perform the measurement, the sample of disintegrated vulcanizate was transferred to a carbon tetrachloride medium, since this solvent possesses an index of refraction appreciably different from that of rubber[9]. Table 1 gives the experimental and calculated data required for computing the coefficient of diffusion and for plotting a standardized diffusion curve (Figure 2).

TABLE 1

DIFFUSION OF DISINTEGRATED VULCANIZATE

Time from start of diffusion, 12,300 seconds

Scale divisions s	Comparator readings S	$s \cdot S$	$s^2 S$	$\xi = \frac{s-\bar{s}}{\sigma}$	$\Phi(\xi) = \frac{\sigma}{\Sigma s} \cdot S$
−10	0	0	0	0	0
− 8	4.5	− 36.0	288.0	−2.48	0.023
− 6	15.5	− 93.0	558.0	−1.88	0.079
− 4	33.5	−134.0	536.0	−1.30	0.171
− 2	55.0	−110.0	220.0	−0.70	0.281
0	90.0	0	0	−0.114	0.461
2	64.5	129.0	258.0	0.474	0.330
4	42.0	168.0	672.0	1.064	0.215
6	20.5	123.0	738.0	1.654	0.105
8	8.0	64.0	512.0	2.244	0.041
10	0.55	5.5	55.0	2.834	0.003
11	0	0	0	0	0

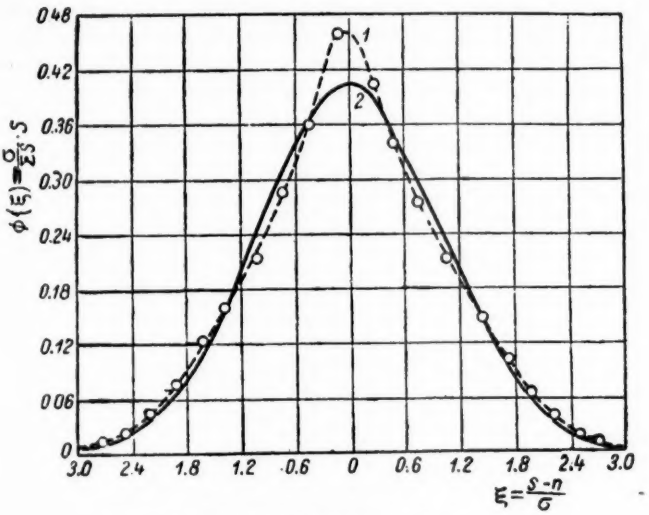

FIG. 2.—Diffusion curve of disintegrated vulcanizate.
1: Standardized experimental curve; 2: Ideal Gauss curve.

The coefficient of diffusion was calculated from the standard deflection:

$$\sigma = \frac{\Sigma s^2 S}{\Sigma s}$$

of the diffusion curve in accordance with the following equation:

$$D = \frac{\sigma^2}{2t} F^2 \qquad (4)$$

where t is the time of diffusion, and F is the projection factor, which equalled 0.435 for the apparatus employed.

From the experimental data:

$$D_1 = \frac{11.51 \times 10^{-2} \times 0.189}{2 \times 1.23 \times 10^4} = 8.84 \times 10^{-7} \text{ sq. cm. per sec.}$$

By substituting this value in Equation (3), we obtain:

$$M = 3600$$

as the molecular weight of the average molecule of disintegrated vulcanizate.

The coefficient of diffusion can also be calculated from the maximum ordinate of the diffusion curve, this calculation leading to the following value:

$$D_2 = 6.62 \times 10^{-7} \text{ sq. cm. per sec.}$$

In the case of a monodisperse material, $D_1 = D_2$. The lack of agreement between these values in our case points to the polydisperse character of the disintegration product. The degree of polydispersion can be characterized by the diffusion coefficient-distribution curve, whose shape, according to Gralen[10],

is logarithmic. This curve is shown in Figure 3. It has a sevenfold to eightfold dispersion, and is more drawn out and flatter than is observed according to Pasynskiĭ's data for unvulcanized rubber. However, the dispersion is less pronounced for the disintegration product of the vulcanizate than for the thermal disintegration product of natural rubber. This is undoubtedly due to the fact that, in the former case, there is a disintegration of the spatial structure characteristic of the vulcanizate, whereas, in the latter case, there is a disintegration of separate linear molecules, the dimensions of which in the original material are already different from one another.

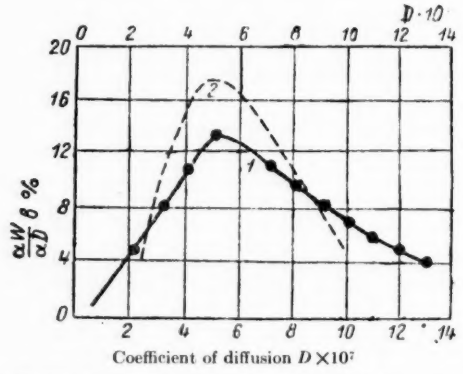

FIG. 3.—Distribution function of diffusion coefficient of disintegrated vulcanizate. 1: Disintegrated vulcanizate; 2: Sol fraction of natural rubber.

By considering the experimentally determined average molecular weight (3600) in conjunction with the axial ratio (1:24) of the disintegrated vulcanizate molecules, it is possible to conclude as a first approximation that these molecules consist, on the average, of four to five mutually interlinked chains containing ten to twelve isopentene groups each. Such an estimate is based on the assumption that the particles of disintegrated vulcanizate are very large, being, so to speak, fragments of the spatial structure of the vulcanizate.

4. MECHANICAL PROPERTIES OF FILMS OBTAINED FROM A DISINTEGRATED VULCANIZATE SOLUTION

To determine the mechanical properties of the disintegrated vulcanizate, the latter was separated from the original solution with acetone; the residue was dried in vacuo at room temperature, whereupon it was redissolved in benzene.

This solution was spread out on a water surface to form thin films, which were tested in a Smirnov dynamometer. The results are presented in Table 2.

TABLE 2

MECHANICAL PROPERTIES OF A VULCANIZATE BEFORE AND AFTER DISINTEGRATION

Name of substance	Tensile strength (kg. per sq. cm.)	Relative elongation (%)
Vulcanizate	190–200	900
Disintegrated vulcanizate	7.2–7.5	250

It is evident that, compared with the original vulcanized rubber, films made from disintegrated vulcanizate have but little mechanical strength, although their elasticity is still considerable. This is only natural when it is considered that the disintegration products are of relatively low molecular weight, and that their molecules are bound together by forces other than those of the molecules of the original vulcanizate. In vulcanized rubber, the molecular chains are bound together by main-valence forces, whereas in disintegrated vulcanizates the individual molecules interact only with the aid of intermolecular attraction forces, the energy of which is smaller than that of main-valence forces by an entire order of magnitude. In any case, our data stand in clear disagreement with the data published by Williams[11], according to which the mechanical strength of vulcanized films before and after peptization is nearly identical.

CONCLUSIONS

1. The product of destructive solution of vulcanizate contains 50 mg. of oxygen per gram of substance; of this quantity, 3.77 mg. falls to the share of oxygen contained in free carboxyl groups.

2. The disintegrated vulcanizate is soluble in ordinary rubber solvents, as well as in binary mixtures of associated and unassociated liquids.

3. The viscosity and light diffusion of a broad range (up to 6 per cent) of disintegrated vulcanizate solutions are linear functions of the concentration.

4. The average molecular weight of the disintegration product of a vulcanizate, as determined from the coefficient of diffusion, is 3600; according to the viscometric and optical data, the molecules represent very large, elongated entities with an axial ratio of 1:24. The distribution curve of diffusion coefficients has a sevenfold dispersion.

5. The mechanical strength and elasticity of films prepared from a disintegrated vulcanizate are very much lower than those of films made of vulcanized rubber.

REFERENCES

[1] Dogadkin and Tarasova, *J. Gen. Chem.* (U.S.S.R.) **17**, 1401 (1947).
[2] Korshun, M. O., Thesis, Inst. Gen. Chem. U.S.S.R. Acad. Sciences.
[3] Barrer, *Trans. Faraday Soc.* **35**, 628 (1939).
[4] Mehl, Oncley, and Simha, *Science* **92**, 132 (1940).
[5] Gotovskaya and Pasynskiĭ, *J. Phys. Chem.* (U.S.S.R.) **20**, 715 (1946).
[6] Novikov, A., Thesis, Moscow Inst. Fine Chem. Technol., **1945**.
[7] Polson, *Kolloid-Z.* **88**, 51 (1939).
[8] Perrin, *J. Phys. Rad.* **1**, 1 (1936).
[9] For details, see Gotovskaya and Pasynskiĭ, *J. Phys. Chem.* (U.S.S.R.) **20**, 715 (1946).
[10] Gralen, *Kolloid-Z.* **95**, 188 (1941).
[11] Williams, *Proc. Rubber Tech. Conf. London*, **1938**, p. 304.

MEASUREMENTS OF DIFFUSION IN RUBBER *

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It is known that high-molecular substances, when under external stress, show peculiar and characteristic effects. Therefore, it seemed only natural to undertake a study of the internal mechanical behavior of such substances, particularly with respect to their internal mobility.

In principle, this internal behavior can be studied in various ways, among which would be the incorporation into the material under investigation of foreign particles, especially particles of molecular dimensions, which would serve as "probes", and the movements of which could be determined. From a practical point of view, this would mean a study of the diffusion[1] of substances dissolved in the particular material under investigation.

Taking advantage of known methods[2] for measuring the diffusion constants of colored substances in liquids, the present investigation was concerned first of all with the development of a procedure with which it would be possible to make diffusion measurements in high-molecular solid media. Weakly vulcanized rubber was found to serve particularly well as a high molecular material for this purpose. As diffusion substances, five compounds were studied: azaobenzene, 1,1′-azonaphthalene, 2,4-dihydroxy-(1,1′-azonaphthalene) diacetate, 2,4-dihydroxy-(1,1′-azonaphthalene) dibenzoate, and 3,3′-dimethoxydiphenyl-4,4′-bis([4-azo]-1-naphthol) dioleate.

The choice and synthesis of these particular compounds was based on three considerations: first of all, the substances must be intensely colored; secondly, they must be fairly soluble in rubber, and thirdly, they were chosen because they were chemically similar, yet considerably different in molecular weight.

The accompanying table summarizes the results of measurements of the compounds mentioned above, while for comparison the diffusion constants of a few representative gases are included[3].

On the basis of these measurements it is possible, without further investigation, to draw certain conclusions regarding the mobility phenomena in solid rubber. A more critical analysis of the data and the theoretical significance of the results will be considered later.

As a means of it interpreting the mobility phenomena, and because it was desired to express the diffusion constants as a function of the size of the diffusing molecules, the experimental constants are plotted against the molecular weights of the diffusing compounds, as in Figure 1. This approach seemed a reasonable one because the compounds studied are closely related chemically, and none contains groups not present in the other compounds of the series which would be expected to have any special effect. For comparison, the diffusion constants[4] of the various substances in water[5] are included in Figure 1.

The data in Figure 1 make evident at once the peculiar characteristics of rubber as a diffusion medium[6]. First of all, although of high molecular weight,

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Experientia*, Vol. 3, No. 12, pages 490–2 (1947).

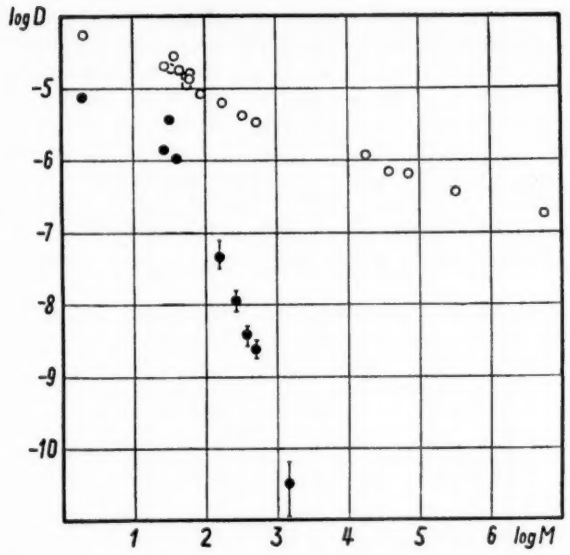

FIG. 1.—Diffusion constant D for the diffusion medium water (○) and rubber (●) as a function of the molecular weight M of the diffusing substances.

DIFFUSION CONSTANTS OF VARIOUS SUBSTANCES IN WEAKLY VULCANIZED RUBBER

Substance	Molecular weight	Diffusion constants* 20°	25°	30°	40°
3,3′-Dimethoxydiphenyl-4,4′-bis([4-azo]-1-naphthol) dioleate	1086	—		—	2.5×10^{-10}
2,4-Dihydroxy-(1,1′-azonaphthalene) dibenzoate	522	2.1×10^{-9}		2.9×10^{-9}	9.6×10^{-9}
2,4-Dihydroxy-(1,1′-azonaphthalene) diacetate	398	2.7×10^{-9}		7.4×10^{-9}	2.6×10^{-8}
Azonaphthalene	282	8.1×10^{-9}		2.0×10^{-8}	3.9×10^{-8}
Azobenzene	182	2.4×10^{-8}			
Carbon dioxide**	44		1.1×10^{-6}		
Nitrogen	28		1.5×10^{-6}		
Oxygen	32		2.1×10^{-6}		
Hydrogen	2		8.5×10^{-6}		

* The diffusion constants are expressed in sq. cm. per second at the four temperatures designated. The values are precise to about 25 per cent. The value for the dianisidine oleate dyestuff is only of the correct order of magnitude.

** The degree of vulcanization of the rubber with which the measurements were made was not known. Since the diffusion constants of gases depend to only a slight extent on the degree of vulcanization, these values can be justifiably included even though the data were obtained with another material.

rubber is distinctly different from ordinary solid substances in that the diffusion constants of the latter are several orders of magnitude smaller. Rubber behaves more nearly like a liquid, particularly with respect to the diffusion through it of substances of low molecular weight. On the other hand, it differs from an "ordinary" liquid, *e.g.*, water[6], in that the diffusion constants decrease notably with increase in the molecular weight of the diffusing substances. As a matter of fact, based on estimates of diffusion constants, Kuhn[1] had already come to these same general conclusions.

With the aid of the Einstein theory of diffusion, it is possible to calculate, from the experimental diffusion constants, the formal viscosities of the diffusion media, just as it is possible to estimate from the mobility of macroscopic substances the viscosity of the medium in which the substances move about. The values obtained in this way (see Figure 2) can be employed for a preliminary characterization of the "liquid" diffusion, media rubber and water.

Water is characterized by the fact that its viscosity is constant and is almost independent of the size[7] of the molecules of the diffusing substances. Moreover, its viscosity is almost the same as the viscosity of water determined in the ordinary way in other experiments.

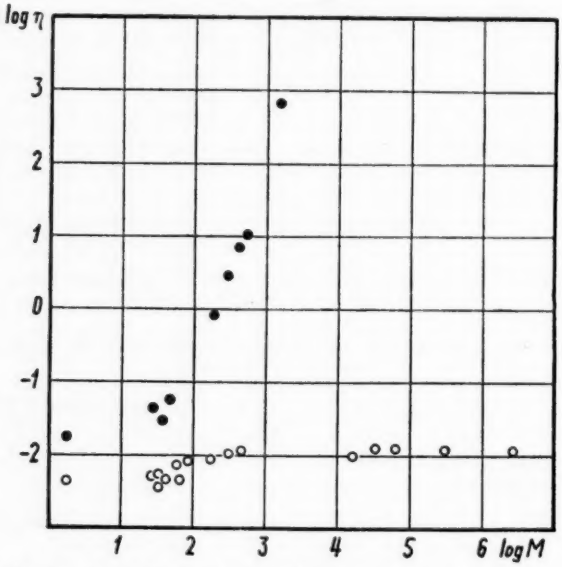

FIG. 2.—Values of the viscosity η, calculated from the diffusion constants, of water (○) and of rubber (●) as a function of the molecular weight M of the substances used for the measurements.

In contrast to this, the "viscosity" of rubber when calculated by the same method depends greatly on the size of the diffusing molecules; in fact, from the diffusion constants of substances with low molecular weights, the calculated viscosities are surprisingly low. However, the values increase considerably with increase in size of the diffusing particles; *e.g.*, from the diffusion constant of a substance with a molecular weight of 1000, a viscosity of 10^3 poises for rubber is obtained.

This variability in viscosity is such as would be expected of substances like rubber on the basis of experimental work by Kuhn and his collaborators[8] on the analysis of the external mechanical behavior of rubber.

On the other hand, the value of 10^3 poises mentioned above for the viscosity of rubber is still considerably smaller than that of 10^6 poises for its normal viscosity when measured externally during slow deformation[9]. From this, and as an extension of earlier conclusions of a similar kind, the direct conclusion may be drawn that, when rubber is deformed in such a way that rubber particles diffuse within the rubber mass itself, the size of these diffusing particles must be

considerable, and therefore that, as required by the statistical theory of the elasticity of rubber, a wide range of thread molecules can move freely within the rubber mass.

SUMMARY

The diffusion constants of various substances in rubber as the diffusion medium were measured. Quantitative determinations of the internal mobility of rubber can be carried out on the basis of the values obtained.

ACKNOWLEDGMENT

The author wishes to thank the Pro Helvetica Society as well as the Foundation for Scholarships in the Field of Chemistry for granting funds which have made it possible to carry out this investigation.

REFERENCES

[1] Kuhn has called attention to the necessity of such measurements, and he himself has already given the order of magnitude of the diffusion constants of phenol with rubber as the diffusion medium, and also has estimated the upper limit of the value of the diffusion constant of the dianisidine dyestuff mentioned in the present work. See Kuhn, Suhr, and Ryffel, *Helv. Phys. Acta* **14**, 497 (1941); Kuhn and Ryffel, *Hoppe-Seylers Z. physiol. Chem.* **276**, 145 (1942).

[2] Special mention should be made of the micromethod of Fürth (*Physik.-Z.* **26**, 719 (1925)).

[3] The diffusion constants of gases in rubber and in similar materials have been known for a long time, and they have been determined by methods other than those employed in the present work. The values given here are from a work of Barrer ("Diffusion in and through Solids", Cambridge, **1941**). For further and newer measurements, see Müller, *Physik.-Z.* **42**, 48 (1941); *Kolloid-Z.* **100**, 355 (1942); Doty, *J. Chem. Physics* **14**, 244 (1945).

[4] In representing these values, all values relating to rubber have naturally been converted to the same temperature (25° C).

[5] These values were taken from work by Höber ("The Physical Chemistry of Cells and Tissues", London, **1946**).

[6] Here rubber is to be regarded merely as one example of a high-molecular substance, just as water, which has been studied particularly well, is an example of an ordinary liquid.

[7] In calculating η, it is assumed, just as in the corresponding calculation for rubber, that the molecules of the diffusing substances are spherical. This assumption is to some extent realized, though a detailed discussion of the subject is withheld at this time.

[8] Kuhn, Künzle, and Preissmann, *Helv. Chim. Acta* **30**, 464 (1947).

[9] Van der Wyk, *Proc. Rubber Tech. Conf. London*, **1938**, p. 985. It has been shown by Kuhn and his collaborators (see *Helv. Chim. Acta* **30**, 307, 464, 839 (1947)) that the viscosity is completely dependent on the frequency of the stress. The given value of 10^6 poises refers to a frequency of approximately 0.05 $sec.^{-1}$.

THE INTERACTION BETWEEN RUBBER AND LIQUIDS. X. SOME NEW EXPERIMENTAL TESTS OF A STATISTICAL THERMODYNAMIC THEORY OF RUBBER-LIQUID SYSTEMS *

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In recent years a number of papers have been published in which the thermodynamic properties of rubber liquid systems have been deduced by statistical methods. These theoretical treatments have on the whole been highly successful, but their critical evaluation is rendered difficult by the almost complete lack of reliable experimental data. Any reasonably comprehensive attempt to fill this gap would be extremely laborious. By concentrating attention on points where, if at all, weaknesses were likely to be found, it has been possible to review fairly quickly the present position.

Calculations of the Gibbs free energy of dilution ΔG_0 of a polymer liquid mixture by the liquid have been based on a lattice model of the system. A lattice point is assumed capable of accommodating either a molecule of solvent or a "segment" of the polymer chain equal in volume to a solvent molecule. An approximate treatment[1] leads to a result of the form:

$$\Delta G_0 = RT \{\ln (1 - v_r) + v_r + \mu v_r^2\} \qquad (1)$$

where v_r is the volume fraction of rubber in the mixture, and μ is a parameter given by:

$$\mu = A + B/RT \qquad (2)$$

where A and B are constants, and Bv_r^2 is the heat of dilution, ΔH_0. The only extensive data at present available to test this result are those for the system: rubber and benzene[2]. The results at 25° C are represented by Equation (1), with only small variations of μ over the whole range of composition, but A and B are both strongly dependent on v_r, especially when this is low[3]. Huggins[4] has shown that Equation (1) describes the rather fragmentary data for a number of rubber-liquid systems at a single temperature. As a result, there is a growing tendency to employ μ as a quantity characterizing a particular polymer liquid mixture. The simplicity of such a procedure makes it very attractive, but it is clearly desirable to apply some critical experimental tests of its validity. This is the purpose of the present paper, and an experimental study has therefore been made of some two-phase equilibria.

The experimental work to be described is largely concerned with vulcanized natural rubber. It is assumed that the introduction of a few cross-links into the rubber has a negligible effect on the heat and entropy of mixing. There is, however, an additional term to be added to Equation (1), representing the decrease of entropy resulting from the network deformation consequent on

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imbibition of liquid. The correction has been evaluated by Flory and Rehner[5] in terms of the molecular weight M_c between junction points of the network. For isotropic swelling they obtain:

$$\Delta G_0 = RT\left\{\ln(1-v_r) + v_r + \mu v_r^2 + \frac{\rho_r V_0}{M_c}\cdot v_r^{\frac{1}{3}}\right\} \tag{3}$$

where ρ_r is the density of the rubber, and V_0 the molar volume of the liquid. If a piece of rubber is constrained to a length l, compared with an initial length l_0 dry and unstrained, Equation (3) must be replaced by:

$$\Delta G_0 = RT\{\ln(1-v_r) + v_r + \mu v_r^2 + \rho_r V_0 l_0/lM_c\} \tag{4}$$

The elastic tension f in the swollen rubber is given[6] by:

$$f = \rho_r A_0 RT(l/l_0 - l_0^2/l^2 v_r)/M_c \tag{5}$$

where A_0 is the cross-section of the dry unstrained rubber. Equation (5) has been shown[7] to hold for highly swollen rubbers, although it is less satisfactory when v_r is large. If, therefore, M_c is estimated from the tension in a highly swollen rubber, there is good reason to expect the last term of Equations (3) and (4) to be accurate for small v_r. Since this term is only important when v_r is small, it is considered that data on vulcanized rubbers may safely be used to test Equation (1).

The quantity measured in the experiments reported below is the equilibrium volume of liquid Q_m imbibed by unit volume of the rubber, and three types of measurement are included. These give the dependence of Q_m on the degree of cross-linking, on the degree of extension l/l_0 of the rubber, and on the temperature. Equations (3) and (4) readily lead to the following expressions for these quantities when the equilibrium condition $\Delta G_0 = 0$ is inserted.

For isotropic swelling, the effect of M_c is given by:

$$\ln(1 + 1/Q_m) - (Q_m+1)^{-1} - \mu(Q_m+1)^{-2} = \rho_r V_0/M_c(Q_m+1)^{\frac{1}{3}} \tag{6}$$

The effect of elongation is given by:

$$\ln(1 + 1/Q_m) - (Q_m+1)^{-1} - \mu(Q_m+1)^{-2} = \rho_r V_0 l_0/lM_c \tag{7}$$

Reference will also be made to some earlier data on the dependence of the tension f on the degree of swelling $Q(=1/v_r - 1)$; an expression for this is obtained from Equation (5):

$$(\partial f/\partial Q)_l = \rho_r A_0 RTl_0^2/l^2 M_c \tag{8}$$

In discussing the experimental data, use is made of the following thermodynamic relations, derivations of which are given in Appendix I.

$$l_0\left(\frac{\partial Q_m}{\partial l}\right)_T = -\frac{V_0}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l \Big/ \left(\frac{\partial \Delta G_0}{\partial Q}\right)_l \tag{9}$$

$$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_{T,f=0} = -\frac{V_0}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l \left\{\frac{1}{l_0 \partial Q_m/\partial l} - \tfrac{1}{3}(Q_m+1)^{-\frac{4}{3}}\right\} \tag{10}$$

$$\Delta H_0 = T\Delta S_0 = -\frac{Q_m}{T}\left(\frac{\partial \Delta G_0}{\partial Q}\right)_T \cdot \frac{\partial \ln(\Delta w)}{\partial 1/T} \tag{11}$$

All the above are true only at $Q = Q_m$. In Equation (11) Δw is the weight of liquid imbibed by a fixed amount of rubber.

Equations (9) and (11) show that the dependence of the maximum swelling on either length or temperature is inversely proportional to $\partial\Delta G_0/\partial Q$. Although the dependence of Q_m on cross-linking is not strictly a thermodynamic problem at all, a simple analysis leads to the conclusion that this also is inversely proportional to $\partial\Delta G_0/\partial Q$. In general, therefore, the variation of Q_m with internal or external parameters is determined by the slope of the free energy-composition curve in the neighborhood of the two-phase equilibrium. It is this fact which makes the ability of an equation to describe these phenomena such a severe test of the theory on which the equation is based.

Effect of cross-linking on swelling capacity.—Several natural rubber vulcanizates were prepared; the compounds, whose compositions are given in Appendix II, being selected to cover a range of "cure". The estimation of M_c was made by allowing a strip of rubber, carrying a dead load, to swell to its maximum capacity in 40/60 petroleum ether at 25° C. When equilibrium was attained, the distance between two reference points on the strip was measured, and the degree of swelling estimated by cutting out the portion of the strip between the reference points and determining its petroleum ether content. The values of 10^{-3} M_c obtained in this way are given in Appendix III; their reciprocals are seen to run roughly parallel with the loads at 300 per cent extension as determined on a standard tensile testing machine (the so-called modulus at 300 per cent). Swelling measurements were carried out in a variety of liquids differing widely both in chemical type and in solvent power. Weighed samples of rubber (about 1 gram) were immersed in excess liquid and maintained at constant temperature for three days, by which time swelling was substantially complete, and then quickly surface-dried, and weighed. The results are shown in Figures 1 and 2, in which Q_m is plotted as a function of $1/M_c$ for the various rubbers, with the addition, for the nonsolvents, of unvulcanized rubber. Data for the two pairs of liquids, chloroform and carbon tetrachloride, benzene and toluene, were so similar that only one of each pair is shown. To fit the data to Equation (6), a value of μ has to be selected to give the best general representation of the points, it being assumed that chemical differences among the rubbers would not be sufficient to affect μ significantly. The curves drawn in Figures 1 and 2 were calculated from Equation (6) by using the values of μ shown in Table I, and evidently give a fairly good representation of the data for the good swelling agents, bearing in mind the difficulty of making satisfactory comparisons of different rubbers. This is in agreement with the conclusion drawn by Flory[8] from his data on the swelling of a range of Butyl rubbers in cyclohexane. The data for methylethyl ketone and ethyl acetate show a systematic deviation from the calculated curve, the effect of cross-linking in reducing the swelling power being more marked than would be expected. It is difficult to estimate the quantitative discrepancy in δQ_m, the amount by which Q_m is lowered by cross-linking, but it would seem that the experimental value for ethyl acetate is at least twice the calculated. It appears rather unlikely that any large part of this factor can arise from the term: $\rho_r V_0/M_c(Q_m + 1)^{\frac{1}{3}}$, since it has previously been found that rubbers swollen by 100 per cent show nearly the theoretical behavior in tension[7]. The tentative conclusion would, therefore, be that $\partial\Delta G_0/\partial Q$ for poor swelling agents is lower than would be expected on the basis of their swelling capacity; in other words, that Equation (1) is only approximately true. The discrepancy involves only small deviations in the value of μ given by Equation (6) when applied to different rubbers. Thus, *e.g.*, Table I gives $\mu = 0.78$ for ethyl

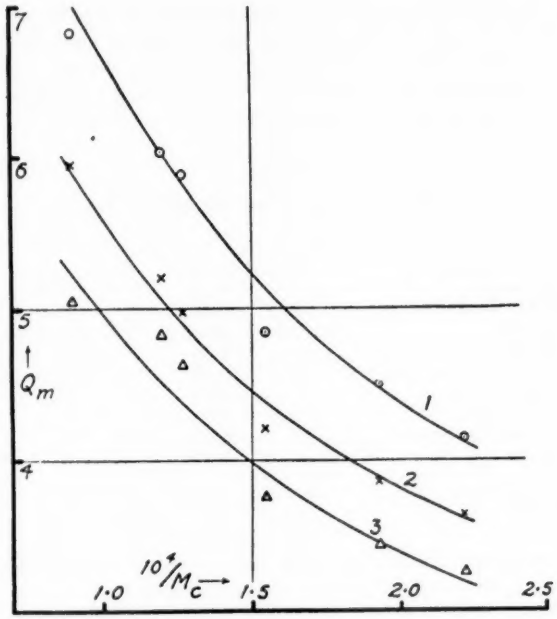


FIG. 1.—Effect of vulcanization on swelling.

(*a*) Good swelling agents. 1. Carbon tetrachloride. 2. Carbon disulfide. 3. Benzene.

(Curves theoretical)

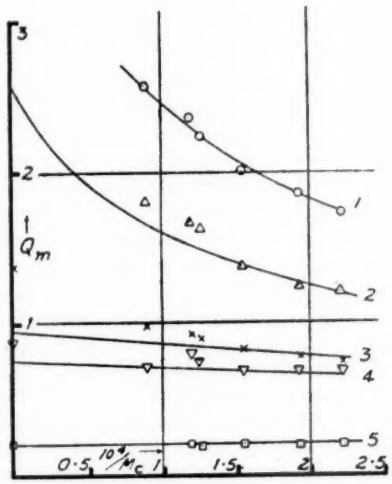


FIG. 2.—Effect of vulcanization on swelling.

(*b*) Moderate and poor swelling agents. 1. 40/60 petroleum ether. 2. *n*-Propyl acetate. 3. Ethyl acetate. 4. Methylethyl ketone. 5. Acetone.

(Curves theoretical)

acetate; the value calculated from the swelling capacity of raw rubber is $\mu = 0.71$. Table I includes for comparison μ values calculated by Huggins[4] from vapor pressure data on raw rubbers, and the general order of agreement is fairly good, suggesting that Equations (1) and (6) are probably both reasonably satisfactory for good swelling agents.

TABLE I

VALUES OF μ FROM EQUATION (6)

Liquid	μ (from Q_m)	μ (vapor pressure)
Carbon tetrachloride	0.29	0.28
Chloroform	0.34	0.37
Carbon disulfide	0.425	0.49
Benzene	0.395	0.43*
Toluene	0.36	0.43–0.44
40/60 petroleum ether	0.54	0.43†
n-Propyl acetate	0.62	—
Ethyl acetate	0.78	—
Methylethyl ketone	0.94	—
Acetone	1.37	—

* Data of Gee and Orr give 0.41.
† Light petroleum.

Effect of extension on swelling.—The measurement of the effect of extension on swelling is in principle much more satisfactory than the comparison of different rubbers. In practice it turns out to be very difficult except for liquids of moderate swelling power. With good swelling agents, only very small extensions can be applied without breaking the specimen, and it becomes necessary to measure relatively small differences in Q_m. In some cases, notably chloroform and toluene, the difficulty is enhanced by failure to attain steady equilibrium values of Q_m, the result obtained increasing very markedly with time[9]. With acetone, the effect of extension on Q_m was very small, but with intermediate liquids, such as ethyl acetate and methyl ethyl ketone, very satisfactory and reproducible results were obtained over a wide range of extensions. Most of the data reported were obtained by stretching rings over glass formers, but for the better swelling agents, there was found to be less danger of rupture if the rubber was stretched in the form of a strip. This latter procedure was more troublesome, as it was necessary to cut out the stretched portion when swollen to equilibrium and determine its swollen weight. The sample was then returned to the liquid to determine its weight when swollen and unstrained, while finally the dry weight was obtained by removing the liquid *in vacuo*. By this method $\partial Q_m/\partial l$ is certainly underestimated for liquids in which Q_m increases with time.

The results are shown in Figures 3 and 4, in which the theoretical curves are calculated from Equation (7), using values of μ chosen to give the observed swelling at $f = 0$. Bearing in mind the above note about chloroform and toluene, Equation (7) is satisfactorily confirmed for good swelling agents (Figure 3). For poor swelling agents, the effect of extension is far larger than predicted. Flory and Rehner[10] have shown that Equation (7) describes accurately the effect of extension on the swelling of a sample of Butyl rubber in xylene.

It is possible to determine whether the unexpectedly large dependence of Q_m on extension arises mainly from anomalies in the elastic behavior or in the state of mixing, by making use of Equation (9), but to do so it is necessary to

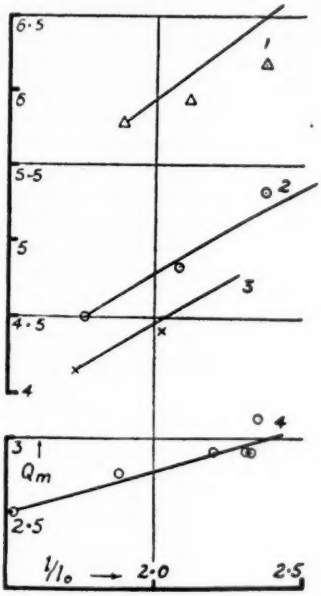


FIG. 3.—Effect of extension on swelling.

Good swelling agents. 1. Chloroform. 2. Benzene. 3. Toluene. 4. 40/60 petroleum ether.

(Curves theoretical)

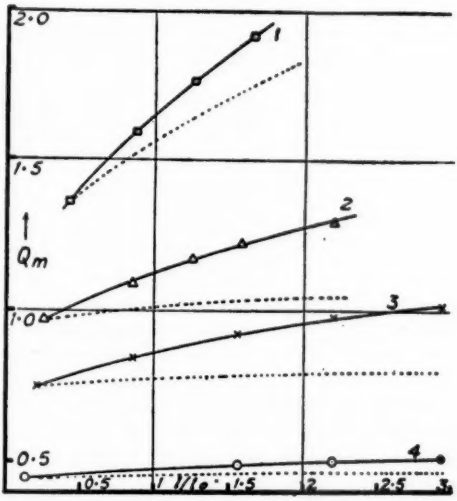


FIG. 4.—Effect of extension on maximum swelling.

Poor swelling agents. 1. *n*-Propyl acetate (add 0.5 to ordinates). 2. Ethyl acetate. 3. Methylethyl ketone. 4. Ethyl formate.

(Dotted curves theoretical)

estimate $(\partial f/\partial Q)_l$. Data have been reported previously[7] on the effect of toluene on the tension of stretched rubber strips; from these $(\partial f/\partial Q)_l$ is readily obtained by graphical interpolation. The resulting figures have been applied to the present data, this being justified by two facts: (1) that similar samples of rubber were used in the two investigations; and (2) that unpublished work[11] has shown that the tension at constant length of swollen rubbers depends, to a first approximation, only on the degree of swelling, and not on the nature of the liquid. It must be emphasized that the figures are not necessarily very precise, since a considerable amount of graphical interpolation has been necessary. Some typical results are given in Table II, in which:

$$l_0 \frac{\partial Q_m}{\partial l}, \qquad -\frac{1}{A_0}\left(\frac{\partial f}{\partial Q}\right) \qquad \text{and} \qquad \left(\frac{\partial \Delta G_0}{\partial Q}\right)_l$$

are compared with values computed from the above statistical equations.

TABLE II

RELATION BETWEEN SWELLING, TENSION AND EXTENSION
(RUBBER A)

Liquid	Q_m (unstrained)	l/l_0	$l_0 \frac{\partial Q_m}{\partial l}$ Expt.	$l_0 \frac{\partial Q_m}{\partial l}$ Theory	$-\frac{1}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l$ Cal./cc. rubber Expt.	$-\frac{1}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l$ Cal./cc. rubber Theory	$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_l$ Cal./mole liquid Expt.	$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_l$ Cal./mole liquid Theory
Ethyl formate	0.447	1.5	0.036	0.0105	0.052_5	0.0310	11_7	237
		2.0	0.025	0.0061	0.036_5	0.0175	11_7	230
		2.5	0.019_5	0.0040	0.027_0	0.0112	11_1	227
Methyl-ethyl ketone	0.75	1.5	0.144	0.0348	0.043_2	0.0310	27	80.1
		2.0	0.119	0.0218	0.025_9	0.0175	22	75.8
		2.5	0.095	0.0138	0.017_6	0.0112	17	73.1
Ethyl acetate	0.96	1.5	0.22_5	0.074	0.039_7	0.0310	17	40.1
		2.0	0.18_7	0.047_5	0.022_8	0.0175	12	36.2
		2.5	0.15_0	0.032_5	0.015_0	0.0112	10	33.7
n-Propyl acetate	1.86	1.5	0.54	0.40	0.033_5	0.0310	7_2	8.9_3
		2.0	0.45	0.30_3	0.018	0.0175	4_6	6.6_7
		2.5	0.36	0.24_6	0.011_5	0.0112	3_7	5.2_4

In considering these results, it must be borne in mind that $\partial Q_m/\partial l$ and $(\partial f/\partial Q)_l$ are both differential quantities, not measured directly, so that both are liable to considerable experimental error. None the less, it is clear from the table that the high values of $\partial Q_m/\partial l$ arise mainly from very low values of $(\partial \Delta G_0/\partial Q)_l$. An important observation is that these low values do not depend essentially on extension, the discrepancy between theory and experiment being of the same order at different extensions. This conclusion is confirmed by extrapolating the data to $f = 0$, and employing Equation (10) to calculate $\partial \Delta G_0/\partial Q$ for the unstretched rubber; the results are set out in Table III. The figures for methylethyl ketone and ethyl acetate are consistent with the observed relatively large effect of vulcanization on the swelling in these two liquids (Figure 2).

By considering the magnitudes of the separate terms in Equation (3) it is easily seen that $(\partial \Delta G_0/\partial Q)_{f=0}$ is determined essentially by the free energy of mixing, no important contribution arising from network deformation. It follows that the last column of Table III gives an estimate of the ratio between

TABLE III

EVALUATION OF $(\partial\Delta G_0/\partial Q)_{f=0}$ (RUBBER A)

Liquid	Q_m	l/l_0 $(=(Q_m+1)^{\frac{1}{3}})$	$-\frac{1}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l$ Cal./cc. rubber	$l_0\frac{\partial Q_m}{\partial l}$	$\left(\frac{\partial\Delta G_0}{\partial Q}\right)_{f=0}$ Cal./mole liquid Expt.	Theory	Ratio expt./ theory
Ethyl formate	0.447	1.13	0.075	0.04_9	120	242	0.50
Methylethyl ketone	0.75	1.20	0.062_5	0.15_9	34	83.9	0.41
Ethyl acetate	0.96	1.25	0.055	0.24_5	21	42.2	0.50
n-Propyl acetate	1.26	1.42	0.037_5	0.55	7_2	8.1_5	0.88

the true and calculated values of $(\partial\Delta G_0/\partial Q)_T$ for raw rubber at the values of Q shown in column 2. It is known by direct measurement that this ratio is close to unity for benzene[2], at all values of Q. The success of the statistical equations in describing both the elastic behavior and the effect of extension on swelling for a series of good swelling agents shows that the same must be true of these. In contrast, the results of Table III suggests that as the limit of imbibition is approached for poor swelling agents, $\partial\Delta G_0/\partial Q$ falls below its calculated value. This has already been shown to be the case for methyl alcohol[12] where, in the neighborhood of maximum swelling, $\partial\Delta G_0/\partial Q$ falls to not more than one-twentieth of the value to be expected from Equation (4) and the observed maximum swelling. Lens' data for acetone[13] are not sufficiently precise to estimate the ratio (observed/calculated) with any precision, but it is certainly low (≈ 0.05). These various observations are collected in Figure 5, in which the ratio of observation to calculation at the point of maximum swelling is plotted as a function of Q_m. There is no reason to expect all the points to lie on a smooth curve, but it seems extremely probable that the curve drawn furnishes at least a rough estimate of the ratio for other liquids. There is, in other words, strong evidence that Equation (1) fails to give the correct dependence of the free energy of dilution on composition for liquids of limited swelling power.

The way in which this failure accounts for some of the anomalous effects of vulcanization and extension on swelling is shown schematically in Figure 6, which relates to a liquid in which raw rubber is swollen to $Q_m = 1.00$. Curves 1 and 2 represent the experimental and calculated curves of ΔG_0 while 3 and 4 give (minus) the increment due to vulcanization, unstretched and stretched to $l/l_0 = 2$. The points of intersection of curves 3 and 4 with 1 and 2 give for the maximum swelling of the vulcanized rubber:

unstretched,	experiment	0.828,	calculated	0.902
stretched,	experiment	0.876,	calculated	0.930

(These figures are, of course, only illustrative, and have no quantitative significance.)

The effect of temperature on swelling.—The temperature dependence of the maximum swelling of several natural rubber vulcanizates was determined in a range of liquids, employing the technique already described. In most cases measurements were carried out in duplicate, the first sample being allowed to swell successively at 0° C, 25° C, 0° C; and the second sample at 25° C, 0° C, 25° C. In this way an adequate check was obtained on the attainment of equilibrium, and the absence of any important drift of Q_m with time. The

results may be expressed in the form $-\partial \ln \Delta w/\partial(1/T)$, where Δw is the weight of liquid imbibed, but to use them to evaluate the heat of dilution from Equation (11), it is necessary also to estimate $(\partial \Delta G_0/\partial Q)_T$. A statistical expression for this quantity obtained from Equation (4) may be used for the good swelling agents. In general, it is necessary to introduce the factor γ, determined in the last section, as the ratio between the true and calculated values of $(\partial \Delta G_0/\partial Q)_T$. From Equation (11), introducing the factor γ, and dividing by v_r^2 gives:

$$\frac{D\Delta H_0}{v_r^2} = \frac{\gamma R}{Q_m + 1}\left(-\frac{\partial \ln \Delta w}{\partial(1/T)}\right)\left\{1 + (1 - 2\mu)Q_m - \frac{\rho_r V_0}{3M_c} Q_m(Q_m + 1)^{5/3}\right\} \quad (12)$$

where Q_m is the mean maximum swelling over the range of temperature considered and μ is determined by Equation (6). The application of this equation to a single rubber in a range of liquids is illustrated in Table IV, values of γ being read from Figure 5. Very similar results have been obtained for other rubbers.

TABLE IV

HEAT AND ENTROPY OF DILUTION FROM TEMPERATURE DEPENDENCE OF SWELLING (RUBBER B)

Liquid	Q_m	$\frac{\partial \ln \Delta w}{\partial(1/T)}$	$\frac{\Delta H_0}{v_r^2}$ Cal./mole liquid	
			Equation (12)	Calorimetric[12] ($Q=0$)
Carbon tetrachloride	6.90	−125	−105	−255
Chloroform	6.81	−185	−130	−450
Carbon disulfide	5.87	35	15	95
Toluene	5.23	30	20	15
Cyclohexane	5.05	75	50	
Benzene	4.96	235	125*	310*
n-Butyl *n*-butyrate	3.25	100	65	
n-Heptane	2.90	75	35	135
di-isopropyl ketone	2.82	330	160	
n-Pentane	2.58	−115	− 45	
n-Butyl acetate	2.39	75	120	
n-Propyl acetate	1.63	620	205	
Ethyl acetate	0.84	1010	230	
Methylethyl ketone	0.62	1000	215	
Methyl acetate	0.30	905	155	
Acetone	0.18	925	120	950

* Direct measurement on raw rubber[3] gives $\Delta H_0/v_r^2 = 310$ at $Q = 0$; 168 at $Q = 4.96$.

Several features of this table call for comment. In the first place the results for the last two members of the series are very largely determined by γ, and it is clear from Figure 5 that this may be quite seriously in error. For the next three members there are direct experimental measurements of γ; for the remainder $\gamma = 1$ is likely to be very nearly accurate.

At first sight the values of $\Delta H_0/v_r^2$ estimated here, do not agree at all well with those based on calorimetric data (compare columns 4 and 5). The discrepancy is always in the direction making the numerical value calculated from the temperature coefficient the smaller of the two. Now it has been shown by direct measurement[3] in the case of raw rubber and benzene that $\Delta H_0/v_r^2$ falls as the benzene content increases, and the value of about 168 calories per mole found at $Q = 4.96$ is in fair agreement with the estimate of 125 obtained here.

For this system the calorimetric estimate, which was based on the heats of mixing of benzene with dihydromyrcene[12], is equal to the experimental value[3] at $Q = 0$. Since both columns 4 and 5 are essentially experimental their disagreement is evidence that $\Delta H_0/v_r^2$ is not independent of the degree of swelling, *i.e.*, that even if μ is independent of composition, the constants A and B of Equation (2) are not.

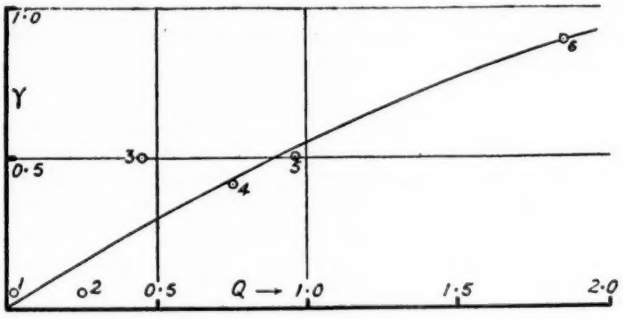
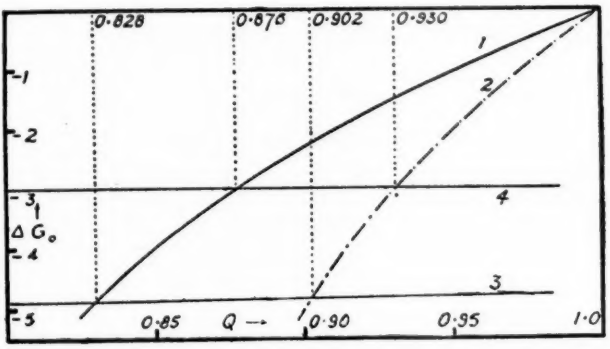


FIG. 5.—Ratio (γ) of experimental to theoretical values of $(\partial \Delta G_0/\partial Q)_T$
1. Methyl alcohol 2. Acetone



FIG, 6.—Theoretical and experimental dependence of Q_m on vulcanization and extension.
1. ΔG_0 raw rubber (exptl.). 2. ΔG_0 raw rubber (theoretical).
3. $-\partial \Delta G_0$ vulcanized rubber at $f=0$. 4. $-\partial \Delta G_0$ vulcanized rubber at $l/l_0=2$.

CONCLUSIONS

The general conclusion which emerges from these experiments is that the simple Equation (1) proposed by Huggins is more limited in application than has been previously supposed. It gives correctly the isothermal dependence on composition of the free energy of a polymer-liquid mixture whose heat of mixing is small, μ being treated as an empirical parameter. It is, therefore, possible to calculate the colligative properties of the mixture at a fixed temperature with fair precision, using only the one adjustable parameter. Since the independence of μ on v_r is found to arise only from an approximately cancellation of the concentration dependence of A and B (Equation 2), the equation cannot be safely used to discuss heats and entropies of dilution. If there is an appreciable

heat of mixing, Equation (1) is no longer strictly accurate even at a fixed temperature. As the polymer approaches saturation, the dependence of ΔG_0 on composition becomes considerably less than expected. The direct consequence of this is that theoretical treatments based on Equation (1) underestimate the extent to which the swelling capacity of a polymer depends on external conditions or structural changes.

Discussion of the origin of these anomalies requires a critical examination of the basis of Equation (1) and of other statistical theories of polymer solutions. This lies beyond the scope of the present paper, and will be considered in a further communication.

SUMMARY

Experimental data are reported on the effects of vulcanization, extension, and temperature on the swelling of rubber. Although in qualitative agreement with a simple equation derived from a statistical theory of polymer solutions, these reveal quantitative discrepancies which are important in discussions of two-phase equilibria.

ACKNOWLEDGMENTS

The author's thanks are due to Miss P. Garnham for experimental assistance, to S. C. Stokes for the preparation of the rubber samples, and to T. A. Sharpley for the modulus determinations. The work described in this paper forms part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

APPENDIX I

THERMODYNAMIC RELATIONS

(*1*) *Dependence of Q_m on extension.*—Considering a stretched, swollen rubber maintained at constant temperature and pressure; by mathematical identity:

$$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_l = -\left(\frac{\partial \Delta G_0}{\partial l}\right)_Q \left(\frac{\partial l}{\partial Q}\right)_{\Delta G_0} \tag{13}$$

and

$$\left(\frac{\partial \Delta G_0}{\partial l}\right)_Q = \left(\frac{\partial}{\partial l}\right)_Q \left(\frac{\partial G}{\partial n_0}\right)_l = \left(\frac{\partial}{\partial n_0}\right)_l \left(\frac{\partial G}{\partial l}\right)_Q = \left(\frac{\partial f}{\partial n_0}\right)_l . \tag{14}$$

where f is the tension in the rubber, and n_0 the number of moles of liquid in the rubber.

Further

$$n_0 = A_0 l_0 Q / V_0 \tag{15}$$

whence

$$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_l = -\frac{V_0}{A_0 l_0} \left(\frac{\partial f}{\partial Q}\right)_l \left(\frac{\partial l}{\partial Q}\right)_{\Delta G_0} \tag{16}$$

A particular case of Equation (16) is obtained by putting $\Delta G_0 = 0$, when $Q = Q_m$ giving:

$$l_0 \frac{\partial Q_m}{\partial l} = -\frac{V_0}{A_0} \left(\frac{\partial f}{\partial Q}\right) \Big/ \left(\frac{\partial \Delta G_0}{\partial Q}\right)_l \tag{9}$$

where the terms on the right are to be given their values at $Q = Q_m$.

(2) *Swelling at constant tension and at constant length.*—Equation (9) may be used to derive the limiting value of $(\partial\Delta G_0/\partial Q)_l$ at $f = 0$. To obtain from this the slightly different function $(\partial\Delta G_0/\partial Q)_{f=0}$, we use the identity:

$$\left(\frac{\partial\Delta G_0}{\partial Q}\right)_{f=0} = \left(\frac{\partial\Delta G_0}{\partial Q}\right)_l + \left(\frac{\partial\Delta G_0}{\partial l}\right)_Q \left(\frac{\partial l}{\partial Q}\right)_{f=0} \tag{17}$$

Now at $f = 0$, $l = l_0(Q + 1)^{\frac{1}{3}}$, so that:

$$\left(\frac{\partial l}{\partial Q}\right)_{f=0} = \tfrac{1}{3} l_0 (Q + 1)^{-\frac{2}{3}} \tag{18}$$

Combining this with the value of $(\partial\Delta G_0/\partial l_0)_Q$ obtained from (14) and (15), and of $(\partial\Delta G_0/\partial Q)_l$ from (9), the final result is:

$$\left(\frac{\partial\Delta G_0}{\partial Q}\right)_{f=0} = -\frac{V_0}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l \left\{ \frac{1}{l_0(\partial Q_m/\partial l)} - \tfrac{1}{3}(Q_m + 1)^{-\frac{2}{3}} \right\} \tag{10}$$

where the quantities on the right are to be given their values at $f = 0$, $Q = Q_m$.

(3) *Temperature dependence of Q_m.*—Considering a swollen rubber at constant pressure, and free from mechanical restraint; by identity:

$$\left(\frac{\partial\Delta G_0}{\partial Q}\right)_T = -\left(\frac{\partial\Delta G_0}{\partial T}\right)_Q \Big/ \left(\frac{\partial Q}{\partial T}\right)_{\Delta G_0} \tag{19}$$

If w_0 is the weight fraction of liquid in the rubber, the entropy of dilution ΔS_0 is given by the well known relation:

$$\begin{aligned} -\Delta S_0 &= (\partial\Delta G_0/\partial T) w_0 \\ &= \left(\frac{\partial\Delta G_0}{\partial T}\right)_Q + \left(\frac{\partial\Delta G_0}{\partial Q}\right)_T \left(\frac{\partial Q}{\partial T}\right)_{w_0} \end{aligned} \tag{20}$$

by identity. If α_0 and α_r are the coefficients of thermal expansion of liquid and rubber, it is easily seen that:

$$\left(\frac{\partial Q}{\partial T}\right)_{w_0} = (\alpha_0 - \alpha_r) Q \tag{21}$$

Substituting in (26) and combining with (25):

$$\Delta S_0 = \left(\frac{\partial\Delta G_0}{\partial Q}\right)_T \left\{ \left(\frac{\partial Q}{\partial T}\right)_{\Delta G_0} - Q(\alpha_0 - \alpha_r) \right\} \tag{22}$$

In the particular case of maximum swelling, $\Delta G_0 = 0$, $Q = Q_m$ and

$$\Delta H_0 = T\Delta S_0 = T\left(\frac{\partial\Delta G_0}{\partial Q}\right)_T \left\{ \frac{\partial Q_m}{\partial T} - Q_m(\alpha_0 - \alpha_r) \right\} \tag{23}$$

In using experimental data obtained by weighing, it is simpler to evaluate the temperature coefficient of the weight increase Δw, and replace Equation (23) by the equivalent expression:

$$\Delta H_0 = T\Delta S_0 = -\frac{Q_m}{T}\left(\frac{\partial\Delta G_0}{\partial Q}\right)_{T, Q=Q_m} \cdot \frac{\partial \ln \Delta w}{\partial(1/T)} \tag{11}$$

APPENDIX II

Composition of Vulcanized Rubbers

	A, A′	B, B′, B″	C	D
Smoked sheet rubber	100	100	100	100
Sulfur	2	3	3	5
Selenium (Vandex)	—	—	2	—
Zinc oxide	2	2	2	2
Stearic acid	0.5	0.5	0.5	0.5
Nonox	0.5	0.5	0.5	0.5
MBTS	1	—	—	—
ZDC	—	1	1	1

APPENDIX III

Cure of Rubbers

	A	A′	B	B′	B″	C	D
Cure (Minutes)	30	30	60	15	30	60	60
at (° C)	142	142	100	142	142	100	100
Modulus (300%) (kg. per sq. cm.)	9	—	24	14	13	28	30
$10^{-3}\,M_C$	8.0	11.1	6.4	7.9	8.3	5.1_5	4.5
10^{-4} Modulus$\times M_C$	(72)	—	155	110	110	145	135

A and A′ differed in the amount of milling received during mixing; A had a bare minimum and was of Mooney viscosity 75; A′ was heavily milled to a Mooney viscosity of 15.

REFERENCES

[1] Flory, *J. Chem. Physics* **10**, 51 (1942); Huggins, *Ann. N. Y. Acad. Sci.* **43**, 1 (1942).
[2] Gee and Treloar, *Trans. Faraday Soc.* **38**, 147 (1942); Gee and Orr, *Trans. Faraday Soc.*, in press.
[3] Gee and Orr, *Trans. Faraday Soc.*, in press.
[4] Huggins, *Ind. Eng. Chem.* **35**, 216 (1943).
[5] Flory and Rehner, *J. Chem. Physics* **11**, 521 (1943).
[6] James and Guth, *J. Chem. Physics* **455** (1943); Flory and Rehner, *J. Chem. Physics* **11**, 521 (1943).
[7] Gee, *Trans. Faraday Soc.*, in press.
[8] Flory, *Chem. Revs.* **35**, 51 (1944).
[9] Scott (*Trans. Inst. Rubber Ind.* **5**, 95 (1929)) has reported that this is a normal feature of swelling, and has termed this relatively slow rise of Q_m the "increment". By working in nitrogen and restricting the duration of experiments, no trouble has been encountered with most of the liquids used.
[10] Flory and Rehner, *J. Chem. Physics* **12**, 412 (1944).
[11] Both by the present author and by L. R. G. Treloar.
[12] Ferry, Gee, and Treloar, *Trans. Faraday Soc.* **41**, 340 (1945).
[13] Lens, *Rec. trav. chim.* **51**, 971 (1932).

FLOW PHENOMENA IN RUBBER. I. FLOW CURVES FOR NATURAL RUBBER *

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INTRODUCTION

Among the various types of plastometer or viscometer which have been applied to the investigation of the flow characteristics of unvulcanized rubber, the shearing-disc viscometer of Mooney[1] is one which most effectively combines the practical requirements of a routine measuring device with some degree of theoretical simplicity. From the theoretical standpoint, however, it suffers from the disadvantage that the rate at which the rubber is sheared is not uniform throughout the volume of the chamber (Figure 1a), but increases with the radial distance from the axis of rotation. It is, therefore, not possible with the standard form of this machine to investigate the dependence of the rate of flow on the shearing stress for substances like rubber which show non-Newtonian flow, *i.e.*, for which the rate of shear is not proportional to the applied stress. This disadvantage was appreciated by Mooney[2], who also designed a concentric cylinder type of viscometer, in which the rate of shear was substantially uniform. This was used for fundamental investigations into the shape of the flow curve.

More recently Piper and Scott[3] devised a simple modification of the shearing-disc viscometer which enables absolute measurements to be made without detracting from the practical convenience of this type of instrument. The modification consists merely in replacing the flat disc by a rotor having two conical surfaces (Figure 1b). By this means a substantially uniform rate of shear is achieved except in the neighborhood of the edge of the rotor. By introducing a suitable correction for this edge region, Piper and Scott were thus able to obtain true flow curves for both natural rubber and GR-S.

In the present work, Piper and Scott's modification has been used to derive more detailed and more extensive information on the flow curves of natural rubber, from which it appears that the shape of the flow curves cannot be satisfactorily represented by the Ostwald–de Waele formula which Piper and Scott employed. In addition, it is shown that from a knowledge of the true flow curve the readings of the standard flat rotor instrument may be approximately predicted. Finally, the effect of temperature on the rate of flow is examined, and is shown to be governed by the normal exponential relation characteristic of liquid viscosities.

EXPERIMENTAL ARRANGEMENT AND DATA OBTAINED

In its essential parts the machine used in these experiments was an exact copy of that described by Piper and Scott, to whose paper reference should be made for dimensional details. The angle between the rotor surface and the

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chamber wall was 0.125 radian (7° 10′). The upper and lower dies were in contact with heavy platens, which were electrically heated and independently thermostatically controlled, the temperature being measured by means of dial thermometers embedded in the platens. The machine was driven by a half horse-power motor through a gear box designed to cover a range of rotor speeds from 0.023 to 12 revolutions per minute in 9 steps each in the ratio 2:1.

The two fixed dies could be removed and replaced by dies of standard pattern when it was desired to work with the normal flat rotor (Figure 1a).

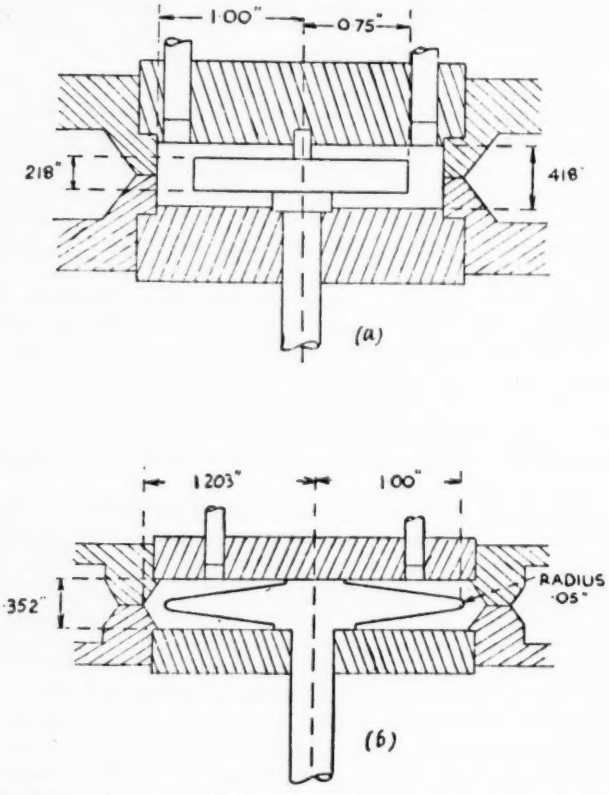

FIG. 1.—The Mooney viscometer. (*a*) Original flat rotor; (*b*) Biconical rotor of Piper and Scott.

A fresh piece of rubber was used for each test at a particular temperature and speed. This was taken from a single batch of smoked sheet which had been softened by mastication on the open mill. The testing procedure was standardized in the following way. With the platens at the desired temperature, the specimen was inserted in the chamber and the dies were closed. After allowing time for heating of the rubber (about 2 minutes) the rotor was driven at a standard speed of 2.98 revolutions per minute for 4 minutes, and the minimum reading during the last revolution was noted. The gear ratio was then adjusted to give the required speed of test, and the machine was run at this speed for two complete revolutions of the rotor, the minimum reading in the second revolution being adopted as the appropriate figure for that particular

temperature and speed. The taking of the minimum reading was facilitated by the addition to the dial gauge of a light pointer which was pushed round by the dial needle.

The object of the preliminary 4-minute run was to bring the rubber into a homogeneous state of flow by working out air bubbles or irregularities introduced during filling. It also provided a check on the reproducibility of the readings for the individual samples under a standard condition. These readings are indicated in Table 1 under the heading "Control".

TABLE 1

DIAL READINGS WITH BICONICAL ROTOR (M′) AND FLAT ROTOR (M)

Temp. (° C)	Biconical rotor												Flat rotor	
Rotor	50°		60°		80°		100°		120°		140°		80°	
speed rev. per min.	Control	M′	Control	M′	Control	M′	Control	M′	Control	M′	Control	M′	Control	M′
0.047	198	50	152	38	125	25	108	15	93	10	78	6	—	—
0.093	205	65	152	53	127	37	108	26	91	16	80	12	56	16
0.187	198	81	147	67	127	52	108	38	93	26	79	19	54	20
0.374	198	102	148	84	128	68	107	52	91	39	79	30	55	28
0.747	196	127	148	101	127	84	109	69	94	55	79	44	56	36
1.49	198	154	149	124	127	103	109	87	95	72	80	60	56	45
2.99	200	195	152	149	127	125	108	107	95	92	80	77	56	56
5.98	—	—	152	175	128	155	108	128	96	113	80	98	56	66
11.96	—	—	151	187	127	177	108	156	92	135	81	120	56	77

Using the conical rotor, the dial reading M′ was obtained over a range of speeds at temperatures of 50°, 60°, 80°, 100°, 120° and 140° C. A set of readings M were also obtained with the standard rotor at a temperature of 80° C. These figures are given in Table I.

DERIVATION OF FLOW CURVES

To derive the flow curves from the dial readings at a particular temperature, the method worked out by Piper and Scott was followed. In this method the total torque is considered to be made up of two contributions, one from the conical region, where the flow is uniform, and one from the edge region, where the flow is not strictly uniform. This second requires an approximate method of analysis, which is based on the assumption of a flow curve obeying the Ostwald–de Waele law:

$$\frac{d\sigma}{dt} = \left(\frac{s}{\eta'}\right)^n \tag{1}$$

$d\sigma/dt$ being the rate of shear, s the shear stress, and η' and n constants. The expression obtained for the torque T then becomes:

$$T = \frac{4}{3}\pi\rho^3 s + 2\pi^2 s X \alpha^{1/n} \tag{2}$$

where s is the stress in the uniform zone, ρ the radius of the rotor, α the angle between rotor surface and chamber wall, and X an instrumental constant which also involves n. The value to be assigned to n in the second (correction) term is obtained by plotting log T against log $(d\sigma/dt)$. In the case where the flow is not governed by Equation (1), we may consider n to be a function of s, and its value in the neighborhood of a particular point may readily be obtained by plotting log $(d\sigma/dt)$ against log T and taking the slope at the point under consideration.

Actually it was found that the edge region accounted for about one-third of the total torque, which indicates quite appreciable departure from the ideal of uniform flow.

Figure 2 represents the set of flow curves on a linear plot, while the same data are shown on a double logarithmic plot in Figure 3. If Equation (1) were applicable, these latter curves should be linear, as found by Piper and Scott. It is seen, however, that they cannot in general be regarded as linear, except over a relatively short range of flow rates. The degree of curvature may of course depend on the rubber used. The relation obtained by Mooney[2] was linear in the stress region below 10^5 dyne per sq. cm., but developed a curvature at higher stresses, comparable with those used in the present experiments.

CONVERSION TO STANDARD ROTOR

Mooney[1] has discussed the method of calculation of the torque developed in the standard (flat) rotor instrument from the absolute flow curve. The calculation is straightforward, involving only a graphical integration of the torque

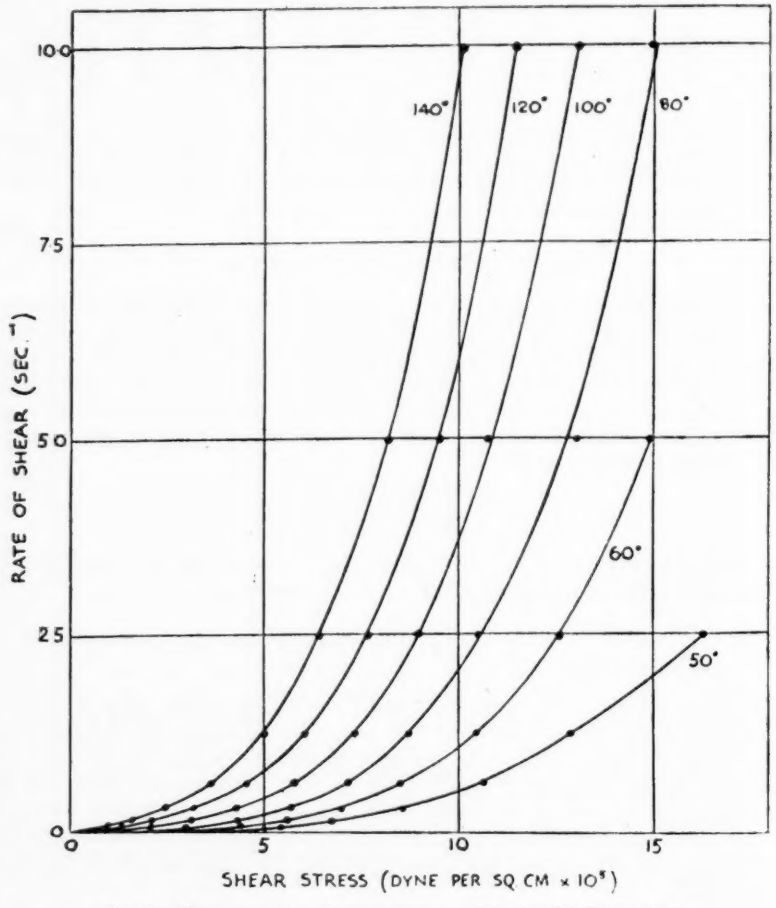

FIG. 2.—Flow curves at various temperatures (Centigrade), linear plot.

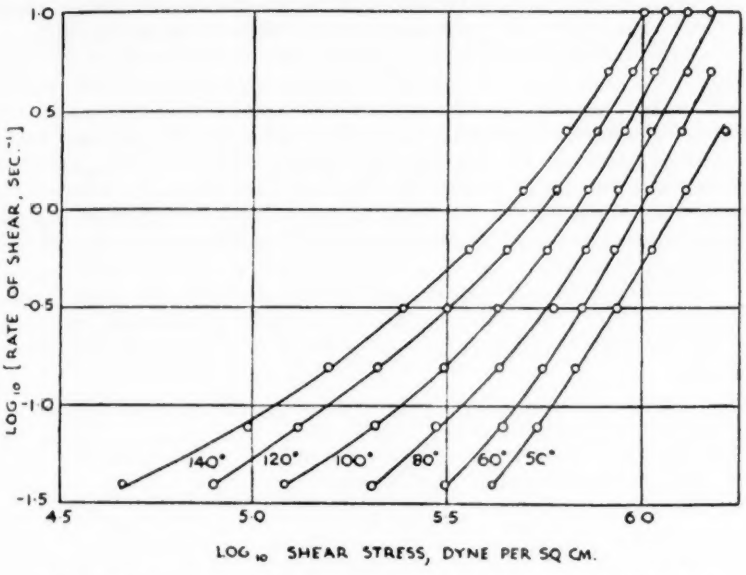

FIG. 3.—Flow curves at various temperatures (Centigrade), double logarithmic plot.

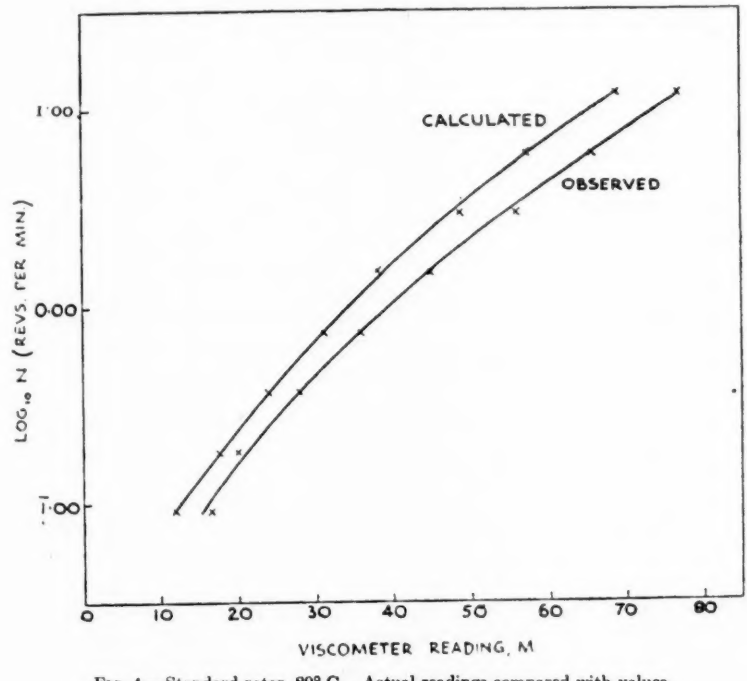

FIG. 4.—Standard rotor, 80° C. Actual readings compared with values calculated from flow curve.

over the rotor surface. The edge difficulty is got over by assuming a plausible effect rate of shear over the edge region. As before, this region gives rise to nearly one-third of the total torque. Figure 4 shows the results of this calculation, which are compared with the directly observed readings at the same temperature. The agreement is not close as might be desired, the calculated values being about 15 per cent lower than those observed. This discrepancy probably arises mainly from the outstanding uncertainty with regard to the state of flow in the edge region, particularly in the case of the flat rotor, where the state of flow is very nonuniform. An error may also arise from the deep grooving of the rotor and stator surfaces, which may well modify the effective clearances to an appreciable extent.

It is interesting to observe that differences of about the same magnitude (up to 14 per cent) were found by Mooney in a comparison of viscosities recorded by the flat-disc instrument with those derived from his cylindrical viscometer.

TEMPERATURE DEPENDENCE

According to Eyring's theory[4], the viscosity of a liquid at low shearing stresses may be represented by the formula:

$$\eta = Ae^{E/RT} \tag{3}$$

where A is a constant and E the "activation energy for flow". This formula has been found to represent with considerable accuracy the temperature dependence of viscosity of most liquids, including long-chain paraffins and polyesters. In the case of rubbers, which are non-Newtonian, the effective viscosity depends on the value of the stress, but a convenient comparison with

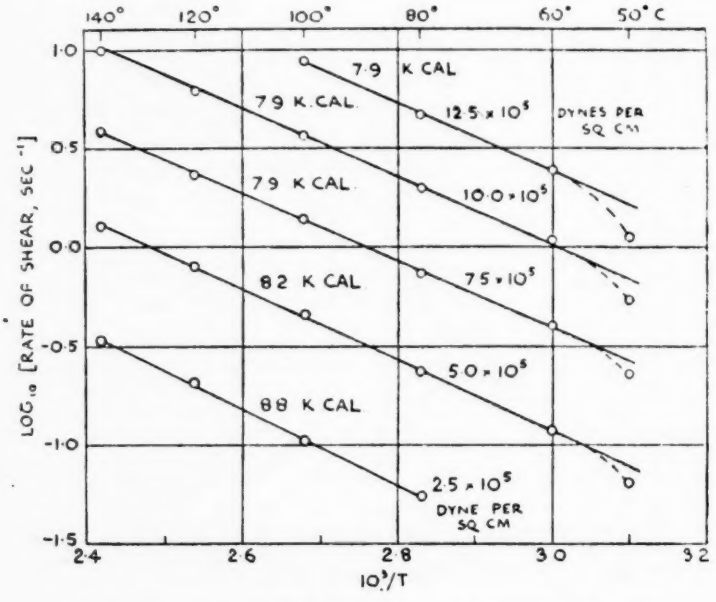

FIG. 5.—Temperature dependence of flow rate at constant stress, showing values of E in equation (3).

the Eyring formula may be made by considering the temperature dependence of the rate of flow $d\sigma/dt$ at a constant value of the shear stress.

In Figure 5 the quantity log $(d\sigma/dt)$ is plotted against the reciprocal of the absolute temperature for a number of different values of the shear stress. The points on these curves were taken from the smoothed curves of Figure 3; they are not direct observations. It is seen that, except at the lowest temperature employed (50° C), these points lie on a set of straight lines, which are very nearly parallel, the actual values of E, determined from the slope, ranging from 7.9 to 8.8, with a mean of 8.1 k. calories per mole. The deviations of the individual values of the slope from the mean are within the probable experimental error; the greatest deviation corresponds to the lowest curve, for which the accuracy was least. There is no evidence of a significant dependence of activation energy on applied stress.

DISCUSSION

Shape of flow curves.—The Ostwald–de Waele law (1), which has frequently been employed to represent the behavior of unvulcanized rubber, is shown from these experiments to be inapplicable except as a rough approximation over a restricted range of rates of flow. This is not particularly surprising, since the law is in any case purely empirical in origin. Further evidence of its restricted range is provided by the observations of Scott and Wharlow[5], using the biconical rotor instrument, which revealed that at very low stresses, namely 10^6 dyne per sq. cm. and lower, the flow was strictly Newtonian.

Temperature coefficient of flow rate.—The mean value of the constant E from the present experiments, 8.1 k. calories per mole, is of the same order of magnitude as the values quoted by Eyring[4] for long-chain paraffins (6 to 7 k. calories per mole), and those obtained by Flory[6] for polyesters of molecular weight ranging from 200 to 10,000 (about 8 k. calories per mole).

It is interesting to compare the present data representing the effect of temperature on the rate of flow with the earlier results obtained by Mooney with the cylindrical viscometer[2]. In Figure 6 the data taken from Mooney's curves for a lightly-milled crepe are reproduced in the same form as Figure 5. The mean activation energy corresponding to the lowest three curves is 7.9 k. calories per mole, which is close to the figure of 8.1 k. calories per mole derived from the present experiments. It is worth noting that this agreement in the E values is found, even though the absolute rates of flow in the two series of experiments differed by a factor of nearly 20, Mooney's sample of rubber being less severely broken down on the mill, and probably, therefore, of a higher mean molecular weight than the authors'. Such an agreement would be in harmony with the basic concept of the Eyring theory, borne out by Flory's experimental work with the polyesters, that the activation energy approaches a constant limit as the chain length of a linear polymer is increased.

The three highest curves of Figure 6 display an increasing degree of irregularity with increasing stress. This suggests that in this region a profound disturbance of the flow process sets in. Similar irregularities were observed in the shearing-disc plastometer by Mooney[1], who suggested that they might indicate the incidence of tearing in addition to laminar flow. Whatever the explanation, it would seem wise to discount the data in this region in any theoretical interpretation of the temperature dependence of flow. Smallwood[7] has interpreted Mooney's data differently, using a more elaborate formula, derived on the basis of Eyring's theory, which accounts for the shape of the flow curves and leads to a dependence of the activation energy on the stress.

Using the Piper and Scott modification of the Mooney viscometer, the flow of masticated rubber has been studied over a range of shear stresses and at a number of temperatures. From these data flow curves, *i.e.*, the relation between the rate of flow and shear stress, at various temperatures, were obtained. The curves do not fit the Ostwald–de Waele relation used by Scott and others.

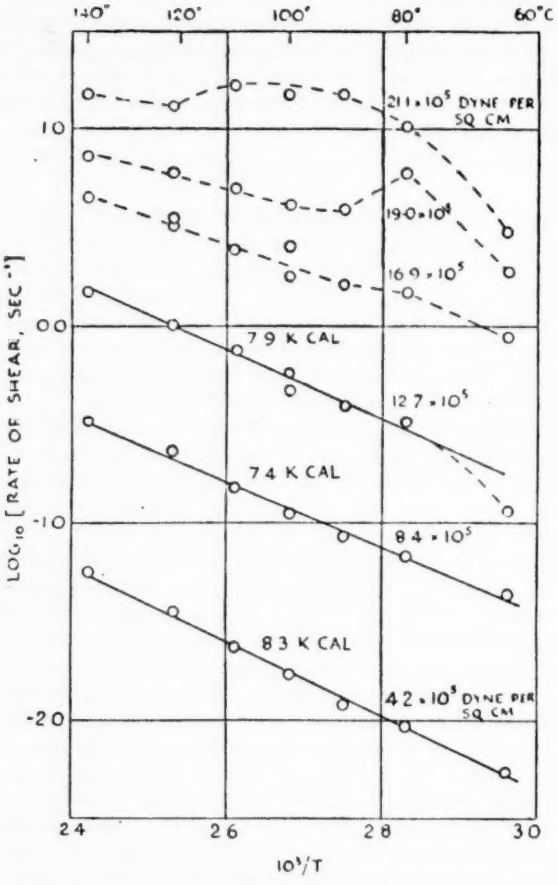

FIG. 6.—Temperature dependence of flow rate at constant stress, from Mooney's data.

SUMMARY

From the flow curves, the readings to be expected in the standard (shearing-disc) Mooney viscometer were calculated. These differ from the observed figures by about 15 per cent.

The temperature dependence of the rate of flow is accounted for on the basis of the simple Eyring formula, and a value of 8.1 k. calorie per mole was obtained for the energy of activation involved in the flow process.

ACKNOWLEDGMENT

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REFERENCES

[1] Mooney, *Ind. Eng. Chem. Anal. Ed.* **6**, 147 (1934).
[2] Mooney, *Physics* **7**, 413 (1936).
[3] Piper and Scott, *J. Scientific Instruments* **22**, 206 (1945).
[4] Glasstone, Laidler, and Eyring, "Theory of Rate Processes", New York, **1941**.
[5] Scott and Wharlow, *Proc. Rubber Tech. Con. London*, **1948**, Paper No. 7, in press.
[6] Flory, *J. Am. Chem. Soc.* **62**, 1057 (1940).
[7] Smallwood, *J. Applied Physics* **8**, 505 (1937).

POLYMERIZATION. VIII. THE ACTION OF METALATING REAGENTS ON RUBBER *

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The Alfin catalysts[1] are metalating[2] as well as polymerizing agents. Hence a knowledge of what metalation does to natural rubber and the Alfin polymer is important. The method used in this study was to subject rubber to the metalating agent, carbonate the product, and examine its solubility in water or other solvents or determine its intrinsic viscosity. Insolubility in organic solvents is taken as evidence of cross-linking. Four reagents were used: alkoxides (as a class), phenylsodium, amylsodium, and 1-pentenylsodium. The first obviously does not add to carbon–carbon double bonds, the second one does not so add[3] and therefore can exert a metalating action only, the third adds to conjugated double bonds[4] but not to monoölefins and is a powerful metalating agent[2], the fourth adds more readily to conjugated bonds[1] than does the third but obviously is a weaker metalating agent. These agents uniformly caused cross-linking in the expected order of metalating strength, which is: amylsodium > phenylsodium > 1-pentenylsodium > alkoxides. The series covers a wide range, from the extremely high activity of amylsodium to the extremely low activity of the alkoxides, the latter so weak that heat and vacuum must be used to remove one component of an equilibrium, after the manner used by McElvain and co-workers[5] in the action of sodium ethoxide on esters. All results are listed in Tables I to IV inclusive, and in each table the order from top to bottom is the order of increasing severity or condition of use. Gel formation follows approximately this same order. A similar series of tests, applied to Alfin polybutadiene and polyisoprene, gave in general similar results (see Table V).

TABLE I

EFFECT OF ALKOXIDES ON NATURAL RUBBER UNDER CONDITIONS THAT SHOULD EFFECT METALATION

Expt.	Alcohol[a]	Max. temp. (° C)	Time[b]	Pressure (microns)	Percentage of product: E	soluble[c] in C	B	insol.[d] in solvents
1	Me_2CHOH	80	11 d	R[e]	60	10	Trace	..
2	EtOH	100	49 h	0.4	60	10	..	7
3	Me_2CHOH	100	46 h	1–50	60	7	20	..
4	Me_2CHOH	100	72 h	1.503.0	20	33	..	4
5	Et_2CHOH	100	45 h	1–50	40	27	13	..
6	$EtMe_2COH$	100	47 h	2.7–15	20	20	..	40
7	EtOH	150	24 h	2–5	13	7	33	53
8	EtOH	150	24 h	1.1–3.2	7	13	20	40
9	Me_2COH	150	24 h	0.7–1.5	13	13	7	53

[a] In this column Me = CH_3, Et = C_2H_5. [b] d = days; h = hours. [c] The solvents used were either (E); chloroform (C) and benzene (B). [d] The blank spaces in these columns may mean that the values were undetermined. The sum of the values is not exactly 100 percent, because of losses or occlusion of solvent. [e] In this experiment the mixture was refluxed in benzene as a solvent.

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TABLE II

EFFECT OF PHENYLSODIUM ON NATURAL RUBBER[a]

Expt.	Cond.[b]	Temp. (° C)	Time (hrs.)	Percentage of product: soluble[c] in E	C	B	insol. in solvents
10	Sta.	R.	24	53	13	3	
11	Sta.	R.	119	13	33		27
12	HSS.	20	5	27	33	3	7
13	HSS.	40	5	13	33	3	33
14	HSS.	60	4.5	4	3		80
15	HSS.	80	5	7	3		80

[a] The amount of rubber used was 0.022 mole, calculated on the basis of the number of C_5H_8 units. The amount of phenylsodium was the same. [b] For the conditions listed in this column, Sta. means standing and HSS. means high-speed stirring. [c] The letters E, C and B refer to ether, chloroform and benzene, respectively.

TABLE III

METALATION OF NATURAL RUBBER BY AMYLSODIUM[a] IN THE HIGH SPEED STIRRING APPARATUS

Expt.	RONa[b] mole equiv.	Temp. (° C)	Time (hrs.)	Percentage of product: soluble[c] in E	C	B	insol. solvents
16	None	20	5	3	3	33	53
17	None	40	2, 3.5[d]	3	3	1	87
18	None	60	5	7	1	1	80
19	None	80	5	3	3		87
20	0.5	20	5	3	3	3	80
21	1.0	20	5	1	3	1	80[e]

[a] The amounts of amylsodium and rubber were 0.044 and 0.022 mole, respectively, the latter being based on the amount of C_5H_8 units present. [b] R = the isopropyl radical. [c] The letters E, C and B refer to ether, chloroform and benzene, respectively. [d] In this experiment the mixture was stirred for two hours, and then allowed to stand for three and one-half hours longer. [e] The gel content of the rubber before solvent extraction was 89 per cent, measured in the conventional manner. The swelling volume of the gel was 11.8. An analysis of the total rubber showed C, 68.7; H, 9.4; Na, 4.4, and O (by difference) 17.5. Small portions of this rubber were alkali water-soluble. The sodium is exceedingly difficult to remove by washing because of the insolubility of the product.

TABLE IV

EFFECT[a] OF 1-PENTENYLSODIUM ON NATURAL RUBBER

Expt.	Molal ratio RNa to R'ONa[b]	Time (hrs.)	Percentage of product: soluble[d] in E	C	insol. in solvents	Gel	S.V.	Int. vis.
	[Control][c]					25	77	2.0
22	None[e]	4	73		10			
23	9/1	5	69		20	36	14	1.4
24	4/1	5	7	7	73	51	19	1.0
25	1/1	5	33	3	33	57	14	1.2
26	1/2	5	1	52	33[f]	58	15	1.4

[a] The amount of 1-pentenylsodium was estimated at 0.044 mole based on a yield of 80 per cent amylsodium and complete utilization in the metalation of 1-pentene. The natural rubber amounted to 0.022 mole, referred to the number of isoprene units. The temperature of reaction was 20° C. The product was carbonated at the end of each reaction but no alkali water-soluble rubber was obtained. [b] R = pentenyl radical; R' = isopropyl. [c] Values for the rubber before treatment with any reagent. [d] E and C have the same meaning as in the previous tables. [e] No isopropoxide was present in the experiment. [f] An ordinary gel determination of the rubber before solvent extraction showed 58.4 per cent gel. Analysis of the rubber before solvent extraction showed C, 57.2; H, 11.2; Na 2.0; O (by difference) 29.6. Analysis of the chloroform-soluble part showed C, 88.4; H, 10.9; O (by difference) 0.7.

TABLE V

EFFECT[a] OF VARIOUS ALFIN CATALYSTS AND ORGANOSODIUM REAGENTS ON ALFIN RUBBERS

Expt.	Polymer[b]	Catalyst[c] or reagent	Gel	S.V.	Intrinsic viscosity
	Polybutadiene	None	7.1	133	3.5
27		PP_1	24.5	30	2.0
28		PP	23.4	20	1.0
	Polyisoprene	None	0	..	9
29		PP[d]	50.3	6	2.3
30		P_2P[d]	40.3	12	2.3
31		Allyl Na[d]	19.3	12	2.8

[a] The reaction took place for five and one-half hours at 20°. [b] The polybutadiene was prepared with a catalyst made from 2-pentanol and 1-hexene, commonly designated as a P_2H_1 catalyst. The polyisoprene was made with the PP or allylsodium–sodium isopropoxide catalyst. [c] The letters refer to the components used in making the catalyst, the first letter to the alcohol and the second to the olefin[1]. PP_1 = Propanol-2 and 1-pentene, respectively. PP = Propanol-2 and propylene, respectively. P_2P = Pentanol-2 and propylene, respectively. [d] Quantities of reagents are not equivalent.

TABLE VI

EFFECT OF ALKALI METAL ON NATURAL RUBBER[a] AT REDUCED PRESSURE

Expt.	Metal (g.)	Max. temp. (° C)	Time[b] at max. temp.	Pressure (microns)	Percentage of product soluble[c] in E	C	B
32	None[d]	Room			80		
33	None	150–170 170–180 180	6 h 30 m 15 m	1–3	47	13	
34	Na 5	150–180	100 m	17–50	40	7	
35	Na 5	150	50 h	0.4–1	27	7	7
36	Na 5	230[e]	25 h	1.7–12	20	13	
37	K 5	180[e]	30 h	1.5–5.5	20	33	

[a] 1.5 g. of rubber was used in each test. [b] m = minutes; h = hours. [c] E = ether, C = chloroform and B = benzene. [d] Control test of the solubility of the rubber. [e] At this temperature the metal vaporized and deposited a mirror in the neck of the flask.

TABLE VII

EFFECT OF SODIUM METAL RUBBER[a] IN THE PRESENCE OF SODIUM ISOPROPOXIDE AND IN THE HIGH-SPEED STIRRING APPARATUS

Expt.	Sodium (mole)	Isopropyl alcohol (mole)	Solvent[b]	Temp. (° C)	Time (hrs.)	Percentage of product: E[c]	soluble in C	B	insol. in solvents	Approx. mol. wt. of E sol. fract.
38	0.088	0.017	B	80	4.5	47	3	7	33	50,000
39	.088	.017	To	109	5.5	73			Tr.	45,000
40	.088	.017	X	140	5	27	33	7	13	25,000
41	.088	.017	Cu	150	5	73	1		3	20,000
42	.30[d]	.1	Cu	150	5	20[e]	40	5	20	2,300
43	.22	.0	Cu	150	5	130[f]				13,000

[a] Rubber 1.5 g. was used. [b] B = benzene; To = toluene; X = xylene; Cu = cumene. [c] E = ether; C = chloroform; B = benzene. [d] Only one gram of rubber was used in this experiment. [e] Some unsaturated (to permanganate) organic acids, soluble in water were obtained also, from this reaction. [f] The yield was over 100% for reasons not yet understood.

Alfin catalysts contain also minute amounts of metallic sodium left over from the initial reaction of sodium with the alkyl halide used in preparing the catalyst. It is necessary to know whether an alkali metal will also cause cross-linking and metalation. Tests of the action of alkali metal on natural rubber under heat and vacuum (Table VI) and in the high-speed stirring apparatus

(Table VII) showed no cross-linking. If any change occurred, it was in the direction of lower molecular weight. Tests of the action of sodium or potassium on comparatively strong hydrocarbon acids, such as fluorene, triphenylmethane, and diphenylmethane, showed that metalation occurred under appropriately vigorous conditions (Table VIII), but only with fair to poor yields, respectively. Similar tests on the less acidic toluene (Table IX) showed that metalation was slight and was not greatly facilitated by the presence of diphenyl- or triphenylmethane. Therefore the traces of metallic sodium present with the Alfin catalyst do not appear to have any influence on the formation of gel.

TABLE VIII

ACTION OF SODIUM AND POTASSIUM METAL ON HYDROCARBONS THAT PROBABLY HAVE A GREATER HYDROCARBON ACIDITY THAN DOES RUBBER

Expt.	Hydrocarbon[a] (g.)		Metal (g.)		Isopropyl alcohol (g.)	Solvent[b]	React. cond.[c]	Temp. (° C)	Time[d]	Product RCO_2H—[e] (%)
44	Tr	5	Na	1	1	B	R	80	4 h	0
45	F	5	Na	1	1	B	R	80	4 d	0
46	F	5	Na	1	1	X	R	138	11 d	0
47	F	3.7	Na	5	13	X	S	138	5 h	0
48	Tr	5.4	Na	5	6.5	X	S	138	5 h	0
49	F	3.7	Na	5	None	X	S	138	5 h	29
50	F	3.7	Na	5	6.5	X	S	138	5 h	77
51	Tr[f] / F	5.4 / 3.7	Na	5	6.5	X	S	138	5 h	0.2 / 64
52	Tr	5.4	K	8.5	None	X	S	138	3.5 h	69
53	Di	3.7	K	8.5	None	X	S	138	2.5 h	3

[a] Tr = triphenylmethane; F = fluorene; Di = diphenylmethane. [b] B = benzene; X = xylene. [c] R = reflux; S = stirred. [d] d = days; h = hours. [e] RCO_2H refers to the carboxylic acid derived from the hydrocarbon being treated with the metal. [f] A mixture of hydrocarbons was used in the hope that metalation of the one present in smaller amount would facilitate metalation of the other.

TABLE IX

METALATION OF TOLUENE AND OTHER HYDROCARBONS BY POTASSIUM METAL IN BOILING TOLUENE FOR FOUR HOURS

Expt.	Hydrocarbon[a] (g.)	K (g.)	Alcohol[b] (g.)	Products, % RCO_2H[c]	Products, % $PhCH_2CO_2H$[d]
54	To	8.5	None		2.7
55	To	8.5	I 6.4		10.
56	To	8.5	sB 8.1		4.9
57	To	8.5	D 10.9		4.2
58	Di 0.4	8.5	I 6.4	99	1.2
59	Di 3.6	5.2	None	98	8
60	Tr 5.4	5.2	None	39	1
61	Tr 5.4	8.5	I 6.5	62	4.1

[a] To = toluene, present as the solvent; Di = diphenylmethane; Tr = triphenylmethane. [b] I = isopropyl; sB = *s*-butyl; D = diethylcarbinol. [c] RCO_2H = the carboxylic acid derived from hydrocarbons other than toluene. [d] The yield was calculated on the basis of the available metal. [e] Attempts to reproduce this result yielded no higher than 4%.

EXPERIMENTS

The experimental methods used are, in general, identical with those described in earlier publications as far as the preparation of phenylsodium[6], amylsodium[2], allylsodium[2] and the Alfin catalysts[1] are concerned. The high-speed stirring apparatus also has been described elsewhere[7]. The natural rubber was a sample of deproteinized material obtained through the courtesy

of J. T. Blake[8]. Intrinsic viscosities and sol gel determinations were carried out in benzene solution by the method commonly used in the work on the rubber project[9].

Rubber and sodium alkoxides.—The usual method was to dissolve 1.5 gram of rubber in benzene, add 2 grams of sodium metal and a small excess of the alcohol. The mixture was allowed to react or was refluxed, if necessary, under an atmosphere of nitrogen for a long time. In Experiment I, Table I, the mixture was poured onto dry ice after refluxing. In the other experiments of the table, benzene and excess alcohol were removed by an aspirator pump, the flask was transferred to a molecular still, and heat and high vacuum were applied as specified in the table. The product was carbonated by admitting carbon dioxide, cooling and adding solid carbon dioxide. When the carbon dioxide had evaporated, 200 cc. of alcohol was added to destroy traces of sodium metal that might still be present and to dissolve soluble sodium salts. After two hours of refluxing, the alcoholic solution was removed and treated with water and acid to recover any soluble portion. The residue was also treated with acid (100 cc. of 6 *N* acid) the acid subsequently removed, the rubber washed free of chlorine ion (silver nitrate test), and the residue refluxed for four hours with 200 cc. of ethyl ether. Filtration of the ether extract through glass wool and evaporation yielded the ether-soluble rubber. The portion insoluble in ether was similarly treated with 100 cc. of chloroform for four hours and the residue from that treatment was extracted with 100 cc. of benzene for four hours.

Phenylsodium and rubber.—Phenylsodium was made from 2.5 grams (0.022 mole) of chlorobenzene and sodium sand in a total volume of 160 cc. of thiophene-free benzene in the usual way. The mixture was forced by nitrogen pressure into a solution of 1.5 grams of rubber in 100 cc. of thiophene-free benzene. The viscous mixture was allowed to stand for the period given in Table II, after which it was forced onto solid carbon dioxide. Subsequent recoveries of rubber were as described in the previous section. The operations with stirring were in general the same as when the mixture was allowed to stand. Other conditions and results are given in Table II.

Amylsodium and rubber.—The quantities of amyl chloride and sodium used for preparing amylsodium were such as to give 0.044 mole in each experiment based on an 80 per cent yield. If isopropyl alcohol was added to this mixture to form the isopropoxide, enough additional amylsodium was prepared to allow for this consumption. Rubber, 1.5 grams, was shredded and added to the reaction mixture. For the reaction at 20° the solvent was pentane; for the higher temperatures it was cyclohexane. The products were handled as before. The results are given in Table III.

Pentenylsodium and rubber.—The preparation of amylsodium was carried out in the usual manner, but with 1-pentene as a solvent[2]. Isopropoxide was obtained when desired by addition of the requisite quantity of isopropyl alcohol to 1-pentenylsodium. Rubber was added and the products separated as described in the previous section. The results are given in Table IV. The gel, swelling volume (S.V.) and intrinsic viscosity were determined by standard methods.

Alkali metals and rubber.—Sodium (5 grams) was shaken in 100 cc. of hot sulfur-free toluene. Rubber (1.5 grams) was then added and dissolved in 60° C. An atmosphere of nitrogen was maintained. After removal of as much of the toluene as possible by use of an aspirator, the remainder was removed under a molecular still. Heat and vacuum was applied as described in Table VI.

Carbon dioxide was then admitted, the reaction mixture cooled, and treated with solid carbon dioxide. The rubber was washed and fractionated as described below. The results are given in Table VI.

Reaction of metals with hydrocarbons.—The hydrocarbon in the quantities specified in Tables VII and VIII was dissolved in 40 cc. of benzene or xylene. Sodium was cut into small pieces and added. Alcohol was added as specified; the mixture was refluxed under an atmosphere of dry nitrogen. After the period of time specified in the table the mixture was carbonated by forcing it onto solid carbon dioxide. Alcohol, 100 cc., was added to destroy the sodium. Water, 13 cc., was then added and the solution heated on a water-bath to evaporate the alcohol. The aqueous solution was extracted with petroleum ether and with benzene and was then acidified with hydrochloric acid. The acid solution was then extracted with three 100-cc. portions of benzene and with three 100-cc. portions of ether.

The procedure was, in general, the same when the mixtures were stirred instead of refluxed. Usually the carboxylic acid precipitated on addition of hydrochloric acid and a single crystallization gave fairly good material. Triphenylacetic acid, recrystallized once from benzene, melted at 256.5–258.5° C (the recorded[10] value is 264–265° dec.), fluorene-9-carboxylic acid, recrystallized once from alcohol, melted at 216–218° C (a recorded[11] value is 220–222°), and phenylacetic acid, as obtained by evaporation of the ether extract, melted at 70–72° C (recorded[12] value 76.7°).

SUMMARY

When metalating agents act on natural or Alfin rubber, gel is formed. The amount of gel increases with the activity of the metalating agent and the severity of the conditions under which it is used.

Metallic sodium or potassium does not cause gel to form in natural rubber. Under very severe conditions these metals metalate the highly active hydrocarbons, fluorene, triphenylmethane and diphenylmethane, in fair to poor amounts, depending on the hydrocarbon, but they metalate toluene only slightly, even under highly favorable conditions.

REFERENCES

[1] Morton, Magat, and Letsinger, *J. Am. Chem. Soc.* **69**, 950 (1947).
[2] Morton and Holden, *J. Am. Chem. Soc.* **69**, 1675 (1947); Morton, Brown, Holden, Letsinger, and Magat, *J. Am. Chem. Soc.* **69**, 2224 (1947).
[3] Morton and Wohlers, *J. Am. Chem. Soc.* **69**, 167 (1947).
[4] Morton, Brown, and Magat, *J. Am. Chem. Soc.* **69**, 161 (1947).
[5] McElvain, *J. Am. Chem. Soc.* **51**, 3124 (1929); Roberts and McElvain, *J. Am. Chem. Soc.* **59**, 2007 (1937); Cox and McElvain, *Organic Syntheses* **17**, 54 (1937).
[6] Morton and Letsinger, *J. Am. Chem. Soc.* **69**, 172 (1947).
[7] Morton and Redman, *Ind. Eng. Chem.* **40**, 1190 (1948).
[8] The authors are greatly indebted to J. T. Blake of the Simplex Wire & Cable Company, Cambridge, Mass., for his coöperation.
[9] Baker, Mullen, and Walker, private communication.
[10] Schmidlin, *Ber.* **39**, 636 (1906).
[11] Friedlander, *Ber.* **10**, 536 (1877).
[12] Huntress and Mulliken, "Identification of Pure Organic Compounds: Order I", John Wiley & Sons, New York, **1941**.

THE REACTION OF SULFUR AND SULFUR COMPOUNDS WITH OLEFINIC SUBSTANCES. IV. THE THERMAL DECOMPOSITION OF ORGANIC POLYSULFIDES, AND ITS CONTRIBUTION TO THE SULFUR OLEFIN-REACTION *

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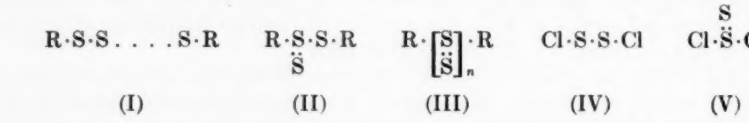
Since polysulfides are the principal products of the reaction of sulfur with olefins[1], an understanding of their thermal stability and of their further reaction with olefins is clearly of importance in clarifying the general problem of chemical changes associated with the olefin–sulfur reaction and the related problem of rubber vulcanization.

The structure of polysulfides has long presented difficulty with respect to the necessity for deciding between their representation by the wholly linear structures (I) or by coördinated structures of type (II) or (III). Based principally on evidence provided by x-ray data[2] and by the lability of a considerable



(I) (II) (III) (IV) (V)

portion of the sulfur atoms on treatment with alkali[3] or with sodium sulfite[4], a coördinated structure has been generally assigned to those polysulfides obtained by the interaction of organic halides and alkali polysulfides. Evidence based on the lability of sulfur atoms is, however, no certain criterion of the presence of coördinated sulfur atoms, since it is now shown that a comparable lability is exhibited by two of the four sulfur atoms in tetrasulfides obtained by the interaction of thiols and sulfur monochloride. Whether one accepts a linear (IV) or branched (V) structure for sulfur monochloride, it follows that three of the four sulfur atoms of the derived tetrasulfide must be in a linear chain, so when two sulfur atoms are removed, at least one of them must have been abstracted from a linear chain. The electron-diffraction investigations of Palmer[5] indicate the linear structure (IV) for the monochloride, and since, moreover, a recent ultraviolet absorption study by Koch[6] provides convincing evidence of a linear structure of some of the organic polysulfides which form the basis of the present work, it seems fully justifiable to assume linear structures both for the tetrasulfides prepared by the interaction of thiols with sulfur monochloride and for the polysulfide products of the sulfur–olefin reaction. The chemical behavior of these polysulfides is not at variance with the assumption of a linear structure, nor is a linear structure inconsistent with the ring formulation of the polymeric organic polysulfides[7].

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The precise mechanism of the removal of sulfur from polysulfides by sodium sulfite or sodium hydroxide is not altogether clear, although, when the former reagent is used, it appears certain that the polysulfide is converted mainly into disulfide[8], although a small proportion (not exceeding 10 per cent) of it undergoes reduction to thiols. Probably there is fission of the sulfur chain, giving thio radicals, which recombine to form disulfides, or, to a small extent, are reduced to thiols, while the sulfur liberated converts sodium sulfite into thiosulfate.

Although the thermal decomposition at 170–180° of some polysulfides containing olefinic unsaturation gives thiols and hydrogen sulfide, together with a sulfurated product of much reduced hydrogen content[1] it is now found that the thermal decomposition of a saturated tetrasulfide at somewhat lower temperatures (140–150°) gives only disproportionation products (lower and higher polysulfides), neither thiol nor hydrogen sulfide being formed. Moreover, at temperatures below 120°, the tetrasulfides could generally be distilled unchanged.

Interaction of a polysulfide $R \cdot S_x \cdot R$ with cyclohexene in the temperature range 140–180° gave sulfurated products of the type $R \cdot S_y \cdot R'$ ($y < x$), in which R was an organic group from the original polysulfide and R′ was cyclohexyl or cyclohexenyl, together with disulfides R_2S_2 derived from the original polysulfide, and cyclohexyl cyclohexenyl di- and poly-sulfides. The latter were similar to the polysulfides resulting from the reaction of sulfur itself with cyclohexene, but contained a smaller sulfur chain. Diethyl tetrasulfide and cyclohexene yielded rather complex mixtures in which the more volatile components could not be adequately separated by distillation, so it was not possible to confirm or to exclude the presence of either the cyclohexanethiol or the cyclohexene episulfide expected from the work of Jones and Reid[9]. The presence of some cyclohexylethyl sulfide was, however, established beyond doubt by the isolation of *cyclohexylethyl sulfone* on oxidation of the most volatile portion of the reaction product. When polysulfides containing larger organic groups were used, the separation of volatile components was facilitated, although the separation of nonvolatile components became correspondingly more difficult. In spite of the most careful search, cyclohexene episulfide could in no case be detected, and the total amount of cyclohexanethiol formed, together with thiols derived from the original polysulfide, was extremely small. The most volatile products in every instance consisted of mixed monosulfides of the type $C_6H_{11}S \cdot R$, R being an organic group of the original tetrasulfide, although when *di*-p-*chlorophenyl tetrasulfide* reacted with cyclohexene some dicyclohexyl sulfide was formed in addition to *p*-chlorophenyl cyclohexyl sulfide. The origin of the dicyclohexyl sulfide in the latter case is obscure.

Unsaturated polysulfides obtained by reaction of sulfur with cyclohexene reacted at 140° with further cyclohexene to give polysulfides with shorter sulfur chains, separable into components, none of which appeared to be of greater sulfur chain-length than a tetrasulfide, with an increasing tendency towards saturation in the more volatile components. The amount of material available did not, however, permit of the isolation of a monosulfide.

It is, accordingly, suggested that the thermal decomposition of polysulfides at temperatures below 180° involves thermal fission of —S—S— bonds. In the absence of a second reactive substance, recombination of fission products regenerates the polysulfides or gives disproportionation products by union of dissimilar fission products. In the presence of an olefin, the fission products (or the thiols derived therefrom by hydrogen capture) may either add to the

ethylenic linkage, forming, ultimately, a saturated sulfide, or the fission product may link with an allylic radical to form an unsaturated mono-, di-, or polysulfide. Simultaneously, reaction occurs between the olefin and sulfur liberated from the sulfur chain of the polysulfide, and since the sulfur may be presumed to be liberated in a rather reactive (possibly atomic) form, the length of the sulfur chain in these products is not large.

It follows that, in the reaction of sulfur with olefins, secondary products resulting from the reaction of primarily formed polysulfides with the olefins are to be expected, especially when the olefin is present in considerable excess. When polysulfides reacted with dihydromyrcene, a considerable quantity of dihydromyrcene cyclic sulfide, identical with that obtained from dihydromyrcene and sulfur[9] (Farmer and Shipley, Part I), was formed. Of particular interest from the point of view of the general reaction of sulfur with polyisoprenes is the ready formation of the cyclic sulfide when dihydromyrcene polysulfide itself was heated with dihydromyrcene, and it is hoped soon to ascertain whether the cyclic sulfide formed in the reaction of polyisoprenes with sulfur is a primary product of the olefin–sulfur reaction, or a secondary product formed solely by interaction of polyisoprene polysulfides with the excess of hydrocarbon usually present in these reactions.

Since it is now generally accepted that rubber vulcanization requires the presence of intermolecular cross-linkages, the combination with rubber of sulfurated fragments of polysulfides alone should not cause vulcanization unless the sulfurated fragments are themselves polyfunctional[10]. Dialkyl tetrasulfides react fairly readily with rubber, giving soluble products containing 2 or 3 units per cent of combined sulfur, which is undoubtedly contained in sulfurated polysulfide fragments added at ethylenic centers of the rubber, since it is well established that products of the reaction of sulfur with rubber, containing considerably less combined sulfur, are quite insoluble. Both the H:C ratio and loss of unsaturation of these tetrasulfide–rubber reaction products are consistent with the postulated incorporation of sulfurated fission products with the rubber; moreover, the product of interaction of di-*p*-chlorophenyl tetrasulfide with rubber contains chemically combined chlorine as well as sulfur. The insolubility of the latter product is attributed to the presence of sulfur in excess of that resulting from simple addition of sulfurated polysulfide fragments, and it appears certain that some degree of cross-linking has been brought about by the reaction of sulfur itself, liberated from the sulfur chain of the polyslufide. These ideas are consistent with Throdahl and Beaver's observation[11] that, although dialkyl tetrasulfides are incapable of vulcanizing rubber, yet some degree of vulcanization is observed with certain aromatic polysulfides.

It is known that, in dehydrogenation reactions at elevated temperatures, disulfides are as effective as sulfur itself, the disulfide linkage undergoing cleavage[12]. If thermal dissociation of disulfides into RS· radicals[13] is appreciable at 140°, then it might be expected that disulfides in the presence of sulfur and an olefin would react essentially as polysulfides, and, furthermore, disulfides themselves might be expected to enter into reaction with olefins. Only scanty evidence of the latter type of reactivity has been obtained with disulfides at temperatures below 180°, and diphenyl disulfide, which might be expected to dissociate rather more readily than dialkyl disulfides, proved to be entirely without action on cyclohexene at 180°. Farmer and Shipley have, however, observed the formation of considerable amounts of mercaptobenzothiazole on heating together benzothiazole disulfide and cyclohexene at 140°. Diethyl disulfide and sulfur, heated together at 140–150°, gave no more than trace

amounts of polysulfide, and when there was also an olefinic substance present, reaction occurred exclusively between the sulfur and the olefin, giving the usual polysulfide products, without any indication of participation of the dialkyl disulfide.

EXPERIMENTAL

Microanalyses were carried out by W. T. Chambers, (Miss) E. Farquhar, and (Miss) H. Rhodes. Olefinic unsaturation was determined by bromine addition[14].

All the experiments with polysulfides were conducted in sealed glass tubes or glass flasks.

Preparation of tetrasulfides.—Tetrasulfides were prepared by a modification of the method described by Bezzi[15]. A 10% solution of sulfur monochloride (1 mol.) in carbon disulfide was added at room temperature to a 10% solution of the appropriate thiol (2.1 mols.) in the same solvent, and as soon as the initial brisk evolution of hydrogen chloride had subsided the solution was gently boiled for 30 minutes under a reflux condenser. The solvent was then removed at room temperature under reduced pressure, and, with the exception of di-*p*-chlorophenyltetrasulfide, which crystallized from the residue, the residual tetrasulfide was finally distilled.

Properties of tetrasulfides.—*Diethyl* (sample A) had b.p. 58–60 /0.1 mm., $n_D^{20°}$ 1.6172; *di-n-butyl* was molecularly distilled at 56° in a falling-film molecular still[16] and had $n_D^{20°}$ 1.5772; *diisoamyl*, molecularly distilled at 56°, had $n_D^{20°}$ 1.5542; *dicyclohexyl*, molecularly distilled at 100°, had $n_D^{20°}$ 1.6050 (Found: C, 49.0; H, 7.45; S, 43.3. $C_{12}H_{22}S_4$ requires C, 48.95; H, 7.55; S, 43.5%); *diphenyl*, molecularly distilled at 110°, had $n_D^{20°} > 1.7$; *di-p-chlorophenyl*, recrystallized from light petroleum, had m.p. 57° (Found: C, 40.65; H, 2.35; Cl, 20.3; S, 36.25. $C_{12}H_8Cl_2S_4$ requires C, 41.05; H, 2.30; Cl, 20.2; S, 36.5). The author is also indebted to F. W. Shipley for a sample (B) of diethyl tetrasulfide, b.p. 45°/0.01 mm., $n_D^{19°}$ 1.610, prepared by interaction of ethyl iodide and sodium tetrasulfide. The proportion of the total sulfur content (hereinafter designated "removable sulfur") removable by a boiling 10% aqueous solution of sodium sulfite was determined for each of these tetrasulfides (Table I).

TABLE I

Tetrasulfide	Removable sulfur (%)	
	3 hrs. at 100°	8 hrs. at 100°
Diethyl (A)	50	50
Diethyl (B)	49	not determined
Di-*n*-butyl	30	45
Diisoamyl	44	50
Dicyclohexyl	11	44
Diphenyl	50	52
Di-*p*-chlorophenyl	50	50

Thermal decomposition of dicyclohexyl tetrasulfide.—The tetrasulfide (17.1 g.) in purified cyclohexane (50 c.c.) was heated for 4 hrs. at 140°, air being excluded. Molecular distillation of the solvent-free product yielded a relatively small amount (2.9 g.) of material of reduced sulfur content which had $n_D^{20°}$ 1.5816 (Found: C, 53.7; H, 8.35; S, 38.0; removable S, 3 hrs., 25.2, 8 hrs., 31.8%), a considerable amount (9.6 g.) of mainly unchanged dicyclohexyl tetrasulfide, $n_D^{20°}$ 1.6032 (Found: C, 49.75; H, 7.55; S, 42.3; removable S, 3 hrs., 9.2; 8 hrs., 37.2%), and a relatively small amount (1.7 g.) of viscous *dicyclohexyl hexasulfide*, $n_D^{20°}$ 1.664 (Found: C, 39.8; H, 6.15; S, 53.7; removable S, 3 hrs., 43.2, 8 hrs.,

49.2. $C_{12}H_{22}S_6$ requires C, 40.2; H, 6.2; S, 53.6%). The infrared spectrum of the hexasulfide revealed no unsaturation.

Reaction of tetrasulfides with olefins.—(1) *Diethyl tetrasulfide and cyclohexene.*—The tetrasulfide (sample A, 20 g.) and cyclohexene (50 cc.) were heated together for 4 hrs. at 140° in the absence of air. After removal of unchanged cyclohexene (34 g.), the product was separated into a wide range of fractions, b.p. 35–75°/0.1 mm. (total weight 18 g.), leaving a viscous residue (6 g.), care being taken to avoid heating above 130° during the distillation. The recovered cyclohexene contained a trace of ethanethiol, but no carbon disulfide could be detected. Redistillation of the volatile portion of the reaction product gave the following main fractions: (i) b.p. 75–77°/13 mm. (3.5 g.), $n_D^{17°}$ 1.5304 (Found: C, 46.05; H, 8.55; S, 46.0; removable S, 2 hrs., 25.9%); (ii), b.p. 77–79°/13 mm. (2.4 g.), $n_D^{17°}$ 1.5388 (Found: C, 42.35; H, 8.05; S, 48.95; removable S, 2 hrs., 28.8%); (iii) b.p. 79°/13 mm. (1.4 g.), $n_D^{17°}$ 1.5490 (Found: C, 38.4; H, 8.25; S, 53.4; removable S, 2 hrs., 30.5%), and (iv) b.p. 55–75°/0.1 mm. (8.4 g.), $n_D^{17°}$ 1.5970 (Found: C, 34.7; H, 6.4; S, 59.3; removable S, 2 hrs., 47.3%). Further fractionation of fraction (iv) gave subfractions of unchanged *n*. Since the H:C ratio of fractions (i), (ii), and (iv) indicated the presence of a considerable proportion of cyclohexyl groups, the most volatile fraction (i) was reduced by sodium in alcohol, whereby di- and polysulfides were converted into sodium mercaptides. Oxidation with acid permanganate of the alkali-insoluble components of the reduced product gave *cyclohexyl ethyl sulfone*, m.p. 34° (Found: C, 54.55; H, 9.30; S, 18.1. $C_8H_{16}O_2S$ requires C, 54.55; H, 9.15; S, 18.2%). The nonvolatile portion of the original reaction product contained mainly cyclohexyl and cyclohexenyl groups (Found: C, 38.6; H, 5.7; S, 54.5; removable S, 4 hrs., 51%). Only a trace of cyclohexanethiol was detected in the reaction product, and no cyclohexene episulfide was isolated.

(2) *Diisoamyl tetrasulfide and cyclohexene.*—The tetrasulfide (17 g.) and cyclohexene (50 cc.) were heated together for 4 hrs. at 180° in the absence of air. Distillation of the reaction product yielded (*a*) unchanged cyclohexene (25 cc.), (*b*) a fraction, b.p. 60–75°/0.01 mm. (21.2 g.), and (*c*) a residue (15.7 g.) not distillable below 100°/0.01 mm. The unchanged cyclohexene was carefully redistilled (Fenske column) and the residue was united with traces of liquid of b.p. < 60°/0.01 mm. isolated during the preliminary separation; the combined liquids (0.5 g.), redistilled at 13 mm., consisted entirely of thiols (Found: C, 64.8; H, 10.4; S, 24.8; active H, 0.75% = 24.0% S as ·SH). Fraction (*b*) was redistilled at 0.1 mm., and yielded mainly *cyclohexyl isoamyl sulfide* (12.5 g.), b.p. 58–60°, $n_D^{20°}$ 1.4860 (Found: C, 70.2; H, 11.6; S, 18.2; removable S, nil. Calc. for $C_{11}H_{22}S$: C, 71.0; H, 12.0; S, 17.2%), together with the following fractions of higher sulfur content: (i) b.p. 60–62° (2.7 g.), $n_D^{20°}$ 1.4909 (Found: C, 69.75; H, 11.45; S, 18.75%); (ii) b.p. 62–65° (0.6 g.), $n_D^{20°}$ 1.5018; (iii) b.p. 65–70° (2 g.), $n_D^{20°}$ 1.5142 (Found: C, 68.55; H, 10.7; S, 20.5%), and (iv) b.p. 70–75° (2.2 g.), $n_D^{20°}$ 1.5218 (Found: C, 65.25; H, 10.2, S, 24.4; removable S, 3 hrs., 12%; *M*, 198; I. V., 46). Permanganate oxidation of the bulk fraction of cyclohexyl isoamyl sulfide gave the sulfone (yield, 60%), m.p. 57–58° (Found: C, 60.25; H, 10.2; S, 14.7%. Calc. for $C_{11}H_{22}SO_2$: C, 60.5; H, 10.2; S, 14.65%), which had mixed m.p. 57° with an authentic specimen of m.p. 57° (Cunneen, this vol., p. 36). The non-distillable residue (*c*) was passed through the molecular still at 56°, at which temperature about half of the material was volatile. The distillate (6.3 g.), a pale yellow mobile oil, had $n_D^{20°}$ 1.5458, and consisted mainly of disulfides (Found: C, 63.8; H, 9.55; S, 26.85; removable S, 8 hrs., 1.5%; *M*, 215). The brown, rather viscous resi-

due (6.1 g.), $n_D^{20°}$ 1.5818, was of greater molecular complexity (Found: C, 61.35; H, 8.4; S, 30.0; removable S, 8 hrs., 10.7%; *M*, 318). Infrared examination of both distillate and residue showed the presence of isoamyl groups, and also revealed the presence of unsaturation of an apparently conjugated type.

A similar experiment conducted at 140° with 12.7 g. of the tetrasulfide gave no cyclohexene episulfide and no more than a trace of thiols. Some cyclohexyl isoamyl sulfide (2.9 g.) was isolated from the crude reaction product; on passing the remainder through the molecular still the volatile portion (7.4 g.), containing considerable unchanged *diisoamyl tetrasulfide*, had $n_D^{20°}$ 1.5481 (Found: C, 48.05; H, 8.55; S, 43.1; removable S, 3 hrs., 37.0; 8 hrs., 43.5% *M*, 250), but the nonvolatile residue (2.1 g.) had $n_D^{20°}$ 1.5958 and probably consisted mainly of cyclohexyl isoamyl polysulfide and cyclohexenylisoamyl polysulfide (Found: C, 43.35; H, 7.0; S, 48.3; removable S, 3 hrs., 45.2; 8 hrs., 53.0%; *M*, 312. Calc. for $C_5H_{11}S_{4.6}C_6H_{10.2}$: *M*, 301). The high proportion of removable sulfur after 3 hrs. at 100° indicates the absence of any appreciable amount of dicyclohexyl tetrasulfide. Treatment of the nonvolatile residue with further cyclohexene for 3 hrs. at 140° gave an increase in weight of 23%, and pot-still molecular distillation of the product gave two fractions of substantially lower sulfur content than the original material; the distillate had $n_D^{20°}$ 1.5358 (Found: C, 56.7; H, 9.3; S, 33.85; removable S, 3 hrs., 28.7; 8 hrs., 30.7%, corresponding to $C_5H_{11}S_{2.5}C_6H_{10.5}$) and the residue had $n_D^{20°}$ 1.6062 (Found: C, 48.95; H, 7.4; S, 42.8; removable S, 3 hrs., 29.7; 8 hrs., 39.2%, corresponding to $C_5H_{11}S_{3.3}C_6H_{10}$.

(3) *Dicyclohexyl tetrasulfide and cyclohexene.*—9.2 g. of the tetrasulfide, heated for 3 hrs. at 180° with excess of cyclohexene, gave 9 g. of dicyclohexyl sulfide free from unsaturation (Found: C, 72.7; H, 11.2; S, 16.2. Calc. for $C_{12}H_{22}S$: C, 72.7; H, 11.15; S, 16.15%), together with higher sulfides containing unsaturation, *e.g.*, a disulfide (5.8 g.), b.p. > 100°/0.01 mm., $n_D^{20°}$ 1.5792 (Found: C, 61.6; H, 8.75; S, 29.3%). Oxidation of the dicyclohexyl sulfide gave *dicyclohexyl sulfone*, m.p. 132.5°, in 80% yield (Found: C, 62.4; H, 9.7; S, 13.65. Calc. for $C_{12}H_{22}O_2S$: C, 62.55; H, 9.65; S, 13.9%).

(4) *Di-p-chlorophenyl tetrasulfide and cyclohexene.*—The product obtained by heating together the tetrasulfide (23.6 g.) and cyclohexene (50 cc.) was separated by one passage through the molecular still at 56° into a pale yellow distillate (A, 14.8 g.) and a golden brown residue (B, 25 g.) which on a second passage through the still at 80° was further separated into a pale yellow distillate (C, 16.0 g.) and a residue (D, 7.3 g.). The distillate A, which had $n_D^{20°}$ 1.5661 (Found: C, 65.9; H, 7.8; Cl, 11.25; S, 15.05%), was redistilled from a flask at 0.001 mm., giving the following fractions: (i) b.p. 72–80° (0.8 g.), $n_D^{20°}$ 1.5252; (ii) b.p. 80–85° (2.0 g.), $n_D^{20°}$ 1.5342 (Found: C, 70.75; H, 9.95; Cl, 3.9; S, 15.3. Calc. for 24.6% $C_{12}H_{15}ClS$ + 73.4% $C_{12}H_{22}S$: C, 69.0; H, 9.80; Cl, 3.9; S, 15.3%), (iii) b.p. 85–92°(2.7 g.), $n_D^{20°}$ 1.5541 (Found: C, 68.45; H, 8.7; Cl, 7.9; S, 15.05. Calc. for 50.5% $C_{12}H_{15}ClS$ + 49.5% $C_{12}H_{22}S$: C, 68.05; H, 8.9; Cl, 7.9; S, 15.1%), (iv) b.p. 92(96° (4.1 g.), $n_D^{20°}$ 1.5762 (Found: C, 65.3; H, 7.05; Cl, 13.95; S, 14.4. Calc. for 89.2% $C_{12}H_{15}ClS$ + 10.8% $C_{12}H_{22}S$: C, 64.5; H, 7.1; Cl, 13.95; S, 14.3%), and a liquid residue (v), not distillable without overheating, $n_D^{20°}$ 1.5808, from which crystallized p-*chlorophenyl cyclohexyl sulfide*, m.p. 25° (Found: C, 63.85; H, 6.8; Cl, 15.75; S, 14.05. $C_{12}H_{15}ClS$ requires C, 63.55; H, 6.7; Cl, 15.65; S, 14.1%). Oxidation of fraction (iv) gave a 62% yield of p-*chlorophenyl cyclohexyl sulfone*, m.p. 68–69° (Found: C, 55.9; H, 5.85; Cl, 13.95; S, 12.4. $C_{12}H_{15}O_2ClS$ requires C, 55.7; H, 5.85; Cl, 13.7; S, 12.4%).

(5) *Cyclohexyl cyclohexenyl polysulfide and cyclohexene.*—A typical polysulfide (Found: C, 34.55; H, 4.85; S, 59.6%), obtained by the action of sulfur on cyclohexene, was heated with an excess of cyclohexene for 3 hrs. at 140°. There was a weight increase of 14% and the product yielded a distillate (pot still) which had $n_D^{20°}$ 1.5805 (Found: C, 56.1; H, 8.1; S, 36.15; removable S, 8 hrs., 33.2%) and a residue which had $n_D^{20°}$ 1.6260 (Found: C, 51.0; H, 7.0; S, 40.9; removable S, 8 hrs., 29.6%).

(6) *Diphenyl tetrasulfide and dihydromyrcene.*—The tetrasulfide (19.1 g.) and dihydromyrcene (50 cc.), heated together for 3 hrs. at 150° in the absence of air, yielded dihydromyrcene cyclic sulfide (3.8 g.) and a reddish brown oil (29.7 g.) which was separated by passage through the molecular still at 80° into a volatile red liquid (21.7 g.) (Found: C, 72.4; H, 7.9; S, 18.7%) which deposited considerable diphenyl disulfide, and a brown viscous residue (4.0 g.) (Found: C, 61.85; H, 7.45; S, 31.7%).

(7) *Dihydromyrcene polysulfide and dihydromyrcene.*—The polysulfide (5.5 g.), obtained by the action of sulfur on dihydromyrcene, and freed from cyclic sulfide and free sulfur by repeated passage through the molecular still, was heated with dihydromyrcene (20 cc.) for 3 hrs. at 145° and yielded 3.3 g. of dihydromyrcene cyclic sulfide, together with 6.5 g. of nonvolatile matter (Found: C, 57.35; H, 8.6; S, 33.35%).

(8) *Tetrasulfides and rubber.*—The tetrasulfides were incorporated into the rubber by milling, the mixtures were heated in sealed evacuated tubes for 3 hrs. at 140°, and the products were extracted with acetone and with chloroform if they were sufficiently insoluble. Diethyl tetrasulfide (0.76 g.) and rubber (5 g.) yielded a reddish brown product (Found: C, 84.8; H, 11.65; S, 2.8%; I.V., 328) which was soluble in benzene and in chloroform. Di-*p*-chlorophenyl tetrasulfide (1.1 g.) and rubber (4 g.) yielded an insoluble product (Found: C, 79.1; H, 10.45; Cl, 2.65; S, 7.25%).

SUMMARY

At temperatures in the region of 140°, organic polysulfides undergo disproportionation resulting from thermal fission of S—S bonds and recombination of the fission products. In the presence of olefins a considerable proportion of the fission products become attached to ethylenic centers of the olefin, forming mixed mono- and polysulfides. The major part of the monosulfide product is fully saturated, hydrogen capture occurring during, or subsequent to the formation of adducts from the olefin and sulfurated fragments; unsaturation, however, appears in the polysulfide portion. The polysulfides are capable of producing monothio cross-links between the original olefinic molecules only in so far as they are able to yield up elementary sulfur to the olefin, and when the original olefin is a polyisoprene, the tendency towards the formation of a high proportion of intramolecular cyclic sulfide still further reduces the opportunity for formation of intermolecular sulfur-cross-linked products.

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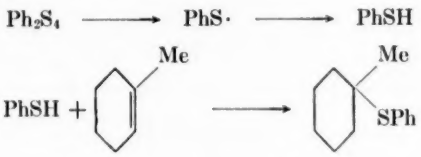
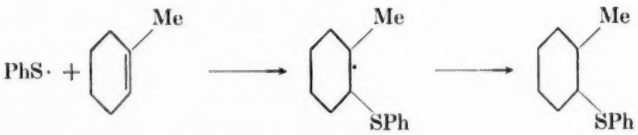
Note added in proof.—Since the above papers were submitted, the reaction mechanism involved in the formation of saturated monosulfides by the inter-

action of polysulfides with olefins has been clarified by a study of the reaction of diphenyl tetrasulfide with 1-methylcyclohexene. Since the major reaction product is phenyl 1-methylcyclohexyl sulfide and not phenyl 2-methylcyclohexyl sulfide, it appears certain that the reaction involves hydrogen capture by the fission product of the polysulfide and addition of the resulting thiol to the double bond by a polar mechanism (I) rather than by a radical addition of the fission product to the double bond followed by hydrogen capture at the other ethylenic carbon atom (II).



(I)



(II)

The structure of the sulfide formed was confirmed by mixed m.p. (76°) of the corresponding sulfone with the phenyl 1-methylcyclohexyl sulfone of m.p. 76° described by Cunneen (*loc. cit.*).

REFERENCES

[1] Farmer and Shipley, *J. Chem. Soc.* **1947**, p. 1519.
[2] Katz, *Trans. Faraday Soc.* **32**, 77 (1936).
[3] Patrick, *Trans. Faraday Soc.* **32**, 347 (1936).
[4] Parker, *India Rubber J.* **108**, 387 (1945).
[5] Palmer, *J. Am. Chem. Soc.* **60**, 2360 (1938).
[6] Koch, in press.
[7] Fuller, *Chem. Revs.* **26**, 160 (1940).
[8] Armstrong, Little, and Doak, *Ind. Eng. Chem.* **36**, 628 (1944).
[9] Jones and Reid, *J. Am. Chem. Soc.* **60**, 2452 (1938).
[10] Patrick, U. S. patent 2,235,621.
[11] Throdahl and Beaver, RUBBER CHEM. TECH. **18**, 110 (1945).
[12] Ritter and Sharpe, *J. Am. Chem. Soc.* **59**, 2351 (1937).
[13] Schönberg, *Ber.* **66**, 1932 (1933).
[14] Bloomfield, *J. Soc. Chem. Ind.* **64**, 274 (1945).
[15] Bezzi, *Gazz. chim. ital.* **65**, 693 (1935).
[16] Farmer and Sutton, *J. Soc. Chem. Ind.* **65**, 164 (1946).

X-RAY STUDIES OF LOW-TEMPERATURE POLYBUTADIENE AND BUTADIENE-STYRENE COPOLYMERS *

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INTRODUCTION

Although it is now generally recognized that the temperature of polymerization affects profoundly the properties of emulsion elastomers, there is very little evidence available pertaining to the cause of the variations of properties. It is felt by some that the improved properties of low-temperature elastomers can be related to variations in molecular weight and molecular-weight distribution. In this laboratory, however, the opinion has prevailed that the lower emulsion polymerization temperatures appreciably alter the fine structure of the molecules with an increase in the regularity of the polymer chains. If there were actually less branching and cross-linking in low-temperature polymers, and less 1,2-addition to monomer components, the increased order should be evident from x-ray diffraction patterns.

To provide information on the above questions, x-ray studies were made with four purposes in view: (1) to determine the effect of polymerization temperature on the crystallization properties of unstretched and stretched polybutadienes; (2) to determine the influence of styrene content on the crystallization of butadiene-styrene copolymers; (3) to study some effects of compounding and vulcanization on crystallizable polybutadiene; and (4) to use the preferred orientation patterns obtained from some of these polymers for structural evaluations. To accomplish these objectives, x-ray patterns were obtained at several temperatures of some unstretched and stretched polybutadiene polymers, butadiene-styrene copolymers, and a vulcanized and compounded polybutadiene. The polybutadienes were prepared by emulsion polymerizations at 55°, 40°, 30°, 20°, 5°, −10° and −20° C. Since the −20° C polybutadiene showed the most marked crystallization patterns, the effects of compounding and of styrene addition were studied, using polymers prepared at this temperature for comparison. Three butadiene-styrene copolymers containing, respectively, 10, 20, and 30 per cent styrene in the monomer charge and one vulcanized polybutadiene compounded with Wyex carbon black were studied.

EXPERIMENTAL

Sample preparation.—The polymers used in the present investigation are given in Table I. All of these samples, with the exception of Nos. 1 and 4, were prepared using a diazothio ether-activated polymerization recipe. No. 1 was prepared using a persulfate recipe; No. 4 using a hydroperoxide-activated system. All of the polymers were modified with long-chain tertiary thiols to

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TABLE I

POLYMERIZATION TEMPERATURE, PERCENTAGE CONVERSION, INHERENT VISCOSITY, AND GEL CONTENT OF EXPERIMENTAL POLYMERS

Sample no.	Type	Polymerization temperature (° C)	Conversion (%)	Inherent viscosity	Gel content (%)
1	Polybutadiene	55	56	2.32	0
2	Polybutadiene	40	89	1.42	57
3	Polybutadiene	30	60	1.64	1
4	Polybutadiene	20	76	1.48	34
5	Polybutadiene	5	65	1.72	47
6	Polybutadiene	−10	61	1.92	0
7	Polybutadiene	−20	60	2.39	0
8	90/10 butadiene/styrene copolymer	−20	60	2.08	0
9	80/20 butadiene/styrene copolymer	−20	63	2.20	0
10	70/30 butadiene/styrene copolymer	−20	58	1.65	1
11	Compounded vulcanizate	−20	60	—	—

the inherent viscosities indicated. Nos. 6 to 10 were prepared in emulsion systems containing antifreeze to depress the freezing point of the aqueous phase below the desired polymerization temperature. Nos. 1 to 6 were pilot-plant samples prepared in 5-gallon reactors. Nos. 7 to 10 were laboratory samples prepared in Crown-capped bottles. The ratios designated for the copolymers are the ratios of the monomers charged. The actual percentages of combined styrene in the copolymers are given in Table II.

TABLE II

STYRENE CONTENT OF COPOLYMERS

Sample no.	Charge ratio	Combined styrene (%)
8	90/10	6.8
9	80/20	16.0
10	70/30	24.0

Although there were some variations in the conversions and molecular wights of these samples, there was no indication that variations within the range indicated by the inherent viscosities affected the diffraction patterns. A careful comparison was made of the diffraction patterns obtained from Sample 7 with those from an otherwise identical sample but having a conversion of only 45 per cent and an inherent viscosity substantially lower. The patterns were identical. This substantiates the conclusion that the molecular weight, within a fairly broad range, is not a significant variable.

Purification of the polymers.—The crude raw polymers were purified by boiling with two successive portions of ethanol–toluene azeotrope, followed by extraction with hot acetone. This type of purification effectively removes nonrubber components as well as a small amount of very low molecular polymer. The extracted samples were transferred to wide-mouth, 2-oz. bottles and placed in a vacuum desiccator. The desiccator was then evacuated for a sufficient length of time to remove traces of solvent. Purified nitrogen, obtained by passing tank nitrogen through a hot tube of copper turnings, was then admitted to the desiccator. The desiccator was then evacuated and flushed four times with purified nitrogen to displace any oxygen held within the sample. After

the desiccator was filled with nitrogen for the last time, the bottles containing the polymer samples were tightly capped and sealed by dipping the capped ends into open paraffin wax. By taking these unusual precautions the samples could be safely stored for a moderate period of time prior to making x-ray measurements.

Preparation of the vulcanized samples.—Although most of the work of the present investigation was carried out using uncompounded polymer, a few measurements were made on compounded and vulcanized samples. Compounding was carried out on a small laboratory mill, using a 50-part loading of channel black. Strips for the x-ray determinations were cut from small slabs of 0.025-inch thickness, vulcanized to a moderate state of cure. The particular compounded sample examined (No. 11 in Table I) was cured for 40 minutes at 307° F, and exhibited a tensile strength of 2470 lbs. per sq. in. at an elongation of 795 per cent.

X-ray technique.—To prepare a homogeneous sample of the purified polymer samples without undue milling and subsequent degradation of the polymer chains, a portion of the purified polymer was subjected to high pressure (5000 to 10,000 lbs. per sq. in.) in a plastic mold. In some instances the mold was heated slightly to cause the material to flow to a substantially homogeneous specimen.

It was observed that as little as 0.1 per cent of antioxidant (phenyl-β-naphthylamine) reduced the detail observable in the diffraction patterns of

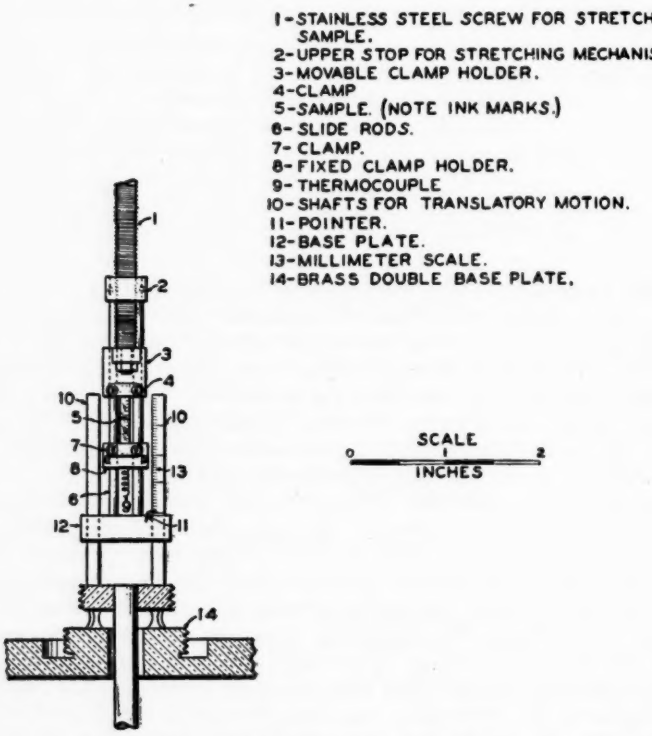


FIG. 1.—Detail of polymer stretching and translation mechanism.

these polymers; therefore, no antioxidant was used in the samples to be described below. Since no antioxidant was used, special precautions were taken to prevent oxidation. The polymers were stored in a darkened desiccator under a carbon dioxide atmosphere. It was found, however, that the effect on the x-ray pattern due to oxidation of the polymer in air at room temperature was negligible over a period of several weeks.

The samples prepared in the press were cut into pieces about 1 × 2 mm. in cross-sectional area and 20 mm. in length. The pieces were placed in a clamp mechanism that permitted exposure in either an unstretched or a stretched condition. Stretching, when desired, was accomplished by separating the clamps using a screw mechanism (Figure 1). Elongations were determined at any given point on the sample by measuring the distance between ink marks which had been placed at 1-mm. intervals along the edge of the unstretched sample. This method was found advisable because the elongations were generally not uniform along a stretched sample.

For purposes of handling and exposing to x-rays at low temperatures, the sample clamp mechanism was placed inside a container composed of two vertical cylinders equipped with Cellophane windows to transmit the diffracted rays

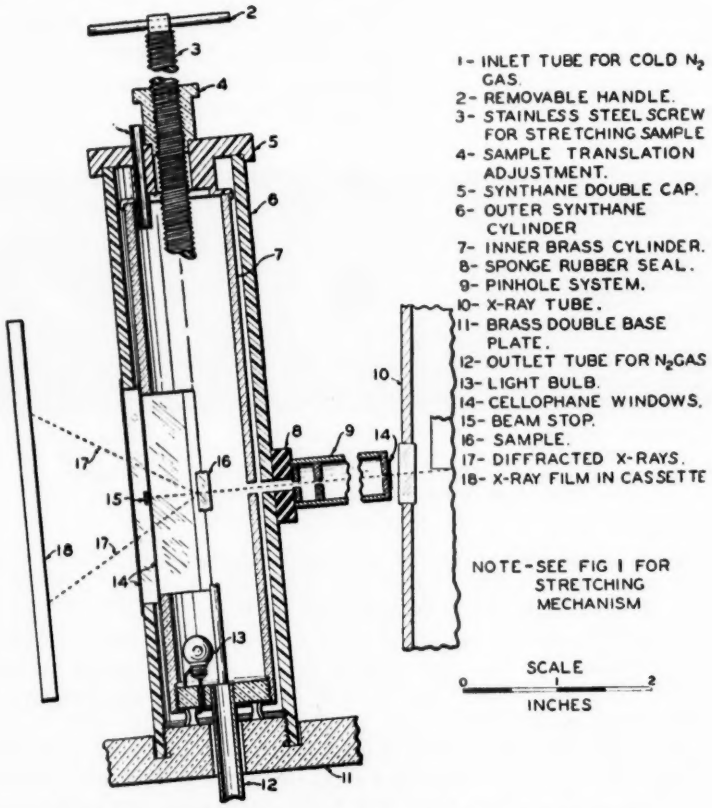
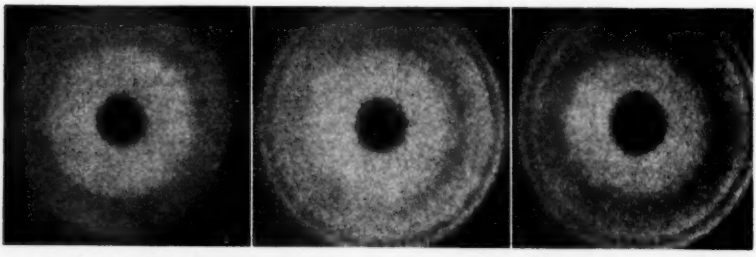


FIG. 2.—Apparatus for obtaining x-ray diffraction patterns of polymers (stretched or unstretched) at low temperatures.

and to permit observation from without (Figure 2). The temperature of the sample was regulated by passing cold nitrogen gas through the sample chamber. The rate of passage was controlled by varying the current to a heater coil immersed in liquid nitrogen contained in a stainless-steel Thermos flask. The temperature of the lower clamp holder was measured by means of a thermocouple, and could be held to ±2.5° throughout the exposure at temperatures down to −100° C. Measurements with a thermocouple imbedded in the center of the sample showed the clamp temperature to be slightly higher than the interior of the sample. The data reported in this work referred to temperatures at the clamp unless otherwise noted. About 15 minutes was required to attain thermal equilibrium. When the apparatus was assembled as described above, the sample could be cooled, stretched, and translated with respect to the x-ray beam. Each of these actions could be performed independently of the others by means of controls outside the sample chamber.

The raw polymer samples were subject to appreciable cold flow when stretched at room temperature and then cooled to 0° C or lower for exposure to x-rays. Patterns obtained in this manner differed only slightly from those obtained from unstretched samples at the same temperature (compare Figure 3*a* with Figure 5*d*). Cooling to 0° C and then stretching, however, gave patterns showing more detail (see Figure 3*b*)[1]. Further cooling of a sample stretched at 0° to −30° C for an x-ray exposure showed a still more detailed pattern than that obtained at 0° (see Figure 3*c*). For most of the results reported on stretched polymer, therefore, the sample was stretched at 0° and then cooled immediately to −30° for exposure to x-rays.



(*a*) Stretched at 25°, x-ray exposure at 0° (*b*) Stretched at 0°, x-ray exposure at 0° (*c*) Stretched at 0°, x-ray exposure at −30°

FIG. 3.—Effect of exposure technique on diffraction patterns of −20° C polybutadiene stretched 300 per cent (flat cassette patterns).

Unfiltered x-rays from chromium or copper target tubes operating at 24 ma. and 30 kv. were used. The x-ray beam was collimated by a pinhole system containing 0.030-inch pinholes as indicated in Figure 2. (A sponge rubber seal between the pinhole system and sample chamber prevented air and moisture from entering the chamber at this point.) After passing through the sample, the main x-ray beam was stopped by a lead button fastened to the inner Cellophane window (Figure 2). A broad stream of air blown across the outer Cellophane window prevented frost formation. Exposures of one hour with a flat cassette and a specimen–film distance of 47.0 mm. were used. Exposure times varying from 1 to 4 hours were used when a cylindrical cassette of 52.0-mm. radius was employed.

DIFFRACTION EFFECTS FOR RUBBERLIKE POLYMERS

The diffraction effects observed for rubberlike polymers as reported in the literature may be classified in three broad groups.

(1) *Diffuse rings* (*halos*) are obtained from polymers that are essentially liquid or are of such a nature that no truly periodic structures are present. The diameter of a halo for a given polymer gives an average distance between a carbon atom in one chain and its closest carbon neighbors in adjacent chains.

(2) *Sharp, uniform diffraction rings* may be obtained from some polymers if a sample is cooled in a suitable manner below its freezing point. Unstretched natural rubber, for example, if properly cooled exhibits such diffraction rings. These rings indicate the presence of small crystalline regions or crystallites randomly oriented throughout the polymer.

(3) *Preferred orientation effects* are usually obtained if polymers that crystallize in the above manner are suitably stretched, since the crystallites tend to line up parallel to the axis of stretching. These effects provide information about the molecular structure of the crystallites. For example, the layer-line patterns obtained from stretched samples indicate the length of the molecular geometrical repeating unit along the polymer chain. Some stretched polymers, however, give preferred orientation effects without true crystallization. This pseudocrystalline effect is probably due to a parallel alignment of the polymer molecules with the stretch axis but with no extended periodicity in other directions. This is indicated in a diffraction pattern by the presence of equatorial spots generally superimposed on the diffuse halo and by the absence of layer-line spots.

All of these characteristic patterns have been observed in the present work and form the basis for discussion that follows.

EFFECTS OF POLYMERIZATION TEMPERATURE ON CRYSTALLIZATION AND PREFERRED ORIENTATION IN POLYBUTADIENE

This section discusses only the influence of polymerization temperature on crystallizability and preferred orientation. Structural deductions that can be made from the patterns described here will be considered later. Data pertaining to these patterns are summarized in Table III, which is discussed more fully in the section on structural analysis.

The polybutadienes described in Table I were examined by x-rays under the following conditions: (1) cooled to −30° C, unstretched; (2) cooled to −70° C, unstretched; and (3) cooled to 0° C, stretched 300 per cent², and cooled to −30° C for exposure.

From the patterns in Figure 4*b* it can be seen that samples of polybutadiene prepared at polymerization temperatures of 40° C and above show no crystallization or preferred orientation effects. Even at −100° C (pattern not shown in Figure 4) the 40° C polymer showed no evidence of crystallization. Crystallization could be induced in unstretched samples prepared at polymerization temperatures of 20° and below (Figure 4*a*). Samples produced at and below 30° showed evidence of preferred orientation when stretched at 0°. Thus it seems that, as the polymerization temperature is increased, the ability of the polymer to crystallize or show preferred orientation effects becomes less and, for these conditions, finally disappears entirely at about 40° C polymerization temperature.

TABLE III

DIFFRACTION DATA FOR −20° C POLYBUTADIENE

Exposure conditions		Behavior of spots in cylindrical cassette patterns: Spot	Equator[a]	Layer line[a]	"d" values (Å)	Relative[a] intensity	Remarks
Purified polymer (No. 7)	Room temperature	—	—	—	4.5	VS	Diffuse halo
		—	—	—	2.24	VW	Diffuse halo[b]
	At −30° C	—	V.	—	10.3	M	Inner rings from flat cassette pattern
		—	V.	—	7.3	W	
		—	V.	—	6.1	VW	
		—	V.	—	3.97	VS	
		a	—	F.	3.22	W	All rings are relatively sharp
		b	—	V.	2.97	M	
		c	—	F.	2.63	VW	
		d	F.	—	2.33	S	
		e	—	F.	2.12	M	
		f	F.	—	1.97	W	
		g	—	V.	1.82	VW	
Compounded polymer (No. 11)	Room temperature	—	—	—	4.5	VS	Diffuse halo
		—	—	—	4.47	M	Sharp ring within diffuse halo
	At −30° C	—	—	—	4.5	W	Diffuse halo
		—	—	—	4.46	S	Sharp ring
		—	—	—	3.97	VS	Sharp ring

[a] V = variable; F = fixed; VS = very strong; S = strong; M = medium; W = weak; VW = very weak.

[b] Probably second order of 4.5 Å halo.

For a given sample, preferred orientation became noticeable at higher temperatures than crystallization in the unstretched condition. On cooling without stretching, the 30° polymer did not crystallize at −70° (Figure 4*b*) and the 20° polymer crystallized at −70° but not at −30°, as shown by the appearance of sharp diffraction rings in the −70° pattern (Figure 4*a*). On the other hand, stretching the 30° polymer at 0° produced faint diffraction spots in a pattern obtained by exposing at −30° (Figure 4*b*).

The patterns of Figure 4(*a* and *b*) show the effect of two temperatures (−30° and −70° C) on the crystallinity of unstretched samples, but do not indicate the exact temperatures at which crystallization could first be detected in the unstretched state. This was done within fairly close limits for the −20° polymer, the crystallinity being observed at 5° but not at 10° (true temperature) as shown in Figure 5. This temperature range was established for 3 different polymer samples prepared at different times but all at −20°.

As the temperature of the polymer was lowered progressively, the intensity of the sharp rings increased, indicating an increasing amount of crystallization. No other changes were observed in the patterns for temperatures down to −70°.

The variation of the diffraction pattern of an unstretched −20° polymer sample kept at 0° for a period of time was studied. No significant difference was found among patterns obtained immediately after cooling, after 20 hours, and after 68 hours at 0° C.

EFFECTS OF COMPOSITION ON CRYSTALLIZATION PROPERTIES

Copolymers of butadiene and styrene prepared at −20° C exhibited the following x-ray diffraction characteristics. The 90/10 copolymer, which crystal-

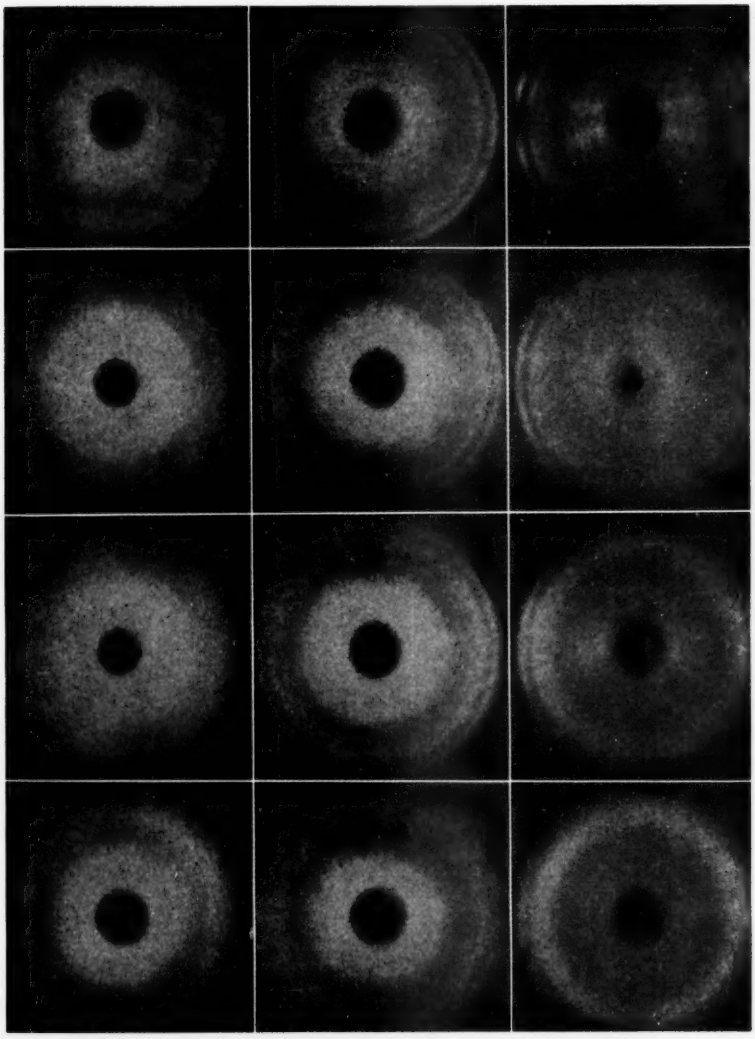


FIG. 4a.—Effect of polymerization temperature on x-ray diffraction patterns of polybutadiene (flat cassette patterns).

lized unstretched at −30° C, contained 6.8 per cent bound styrene and showed preferred orientation effects on stretching at 0° and cooling to −30°, but to a lesser degree than pure −20° polybutadiene under similar conditions (see Figure 6). The 80/20 (16 per cent bound styrene) and 70/30 (24 per cent bound styrene) copolymers polymerized at −20° did not crystallize or show preferred orientation effects under the above conditions. This suggests that the styrene groups do not enter the crystalline regions in the polymer. In the copolymer containing 16 per cent bound styrene, the styrene groups probably

appear frequently enough along the polymer chains to prevent any crystallization that can be detected by x-rays.

EFFECTS OF COMPOUNDING AND VULCANIZATION ON CRYSTALLIZATION PROPERTIES OF −20° C POLYBUTADIENE

The −20° C polybutadiene vulcanizate, when stretched above 400 per cent at room temperature, gave diffraction patterns showing diffuse equatorial arcs on the diffuse halo similar to those given by Morris and Jordan for Buna-S[3] (see Figure 7a). Cooling to 0° and lower produced a sharp diffraction ring giving a spacing slightly smaller than that of the diffuse halo (see Figure 7c) and equal to that given by the strongest diffraction ring of the highly purified polymer at −30°. Stretching at room temperature or lower followed by cooling to 0° or lower caused this sharp ring to break up into sharp equatorial arcs (Figure 7b). The inner rings of the pattern from the compounded vulcanizate are probably due to compounding ingredients. On the other hand the inner rings given by the highly purified polymer (which differ from those given by the compounded and vulcanized polymer) seem to be characteristic of the

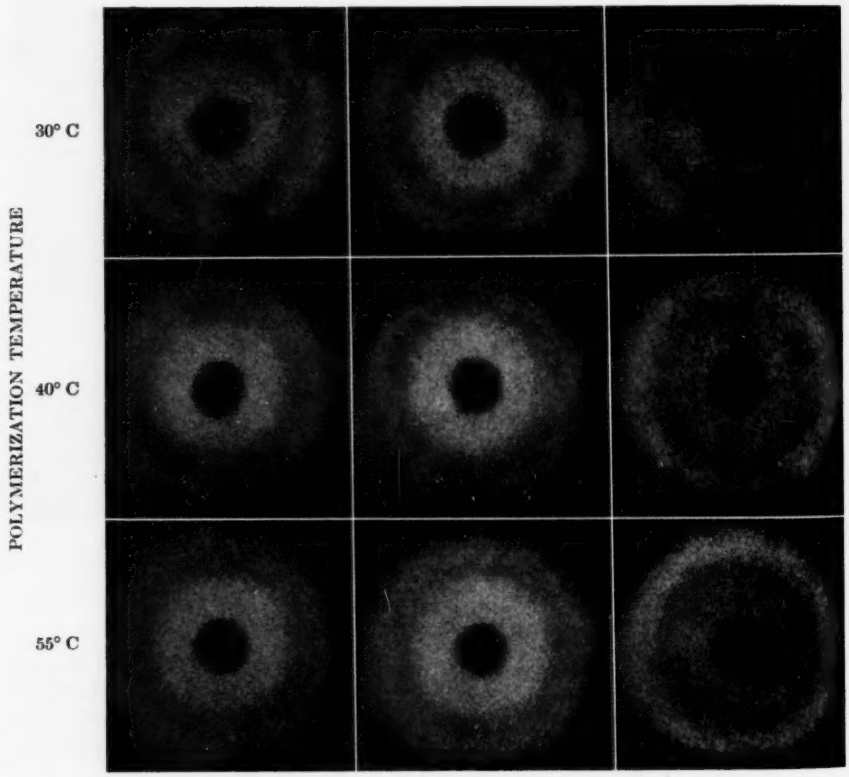
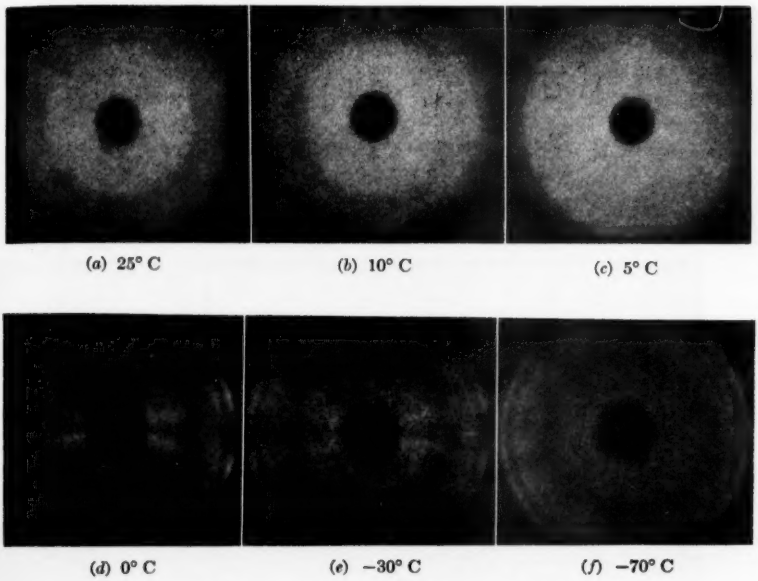


FIG. 4b.—Effect of polymerization temperature on x-ray diffraction patterns of polybutadiene (flat cassette patterns).



(*a*) 25° C (*b*) 10° C (*c*) 5° C

(*d*) 0° C (*e*) −30° C (*f*) −70° C

FIG. 5.—Effect of temperature on crystallinity of unstretched −20° C polybutadiene (flat cassette patterns).

polymer itself. The *d* values given by these rings are, therefore, included in Table III. A peculiarity observable in patterns of the unstretched and stretched compounded polymer at both room temperature and lower was a fairly sharp ring within the diffuse halo.

The detail observable in diffraction patterns of −20° polybutadiene compounded with carbon black was less than that observed in patterns of pure −20° polybutadiene. This is to be expected, however, because of the cross-linking effects occurring during vulcanization and because the carbon black particles impede the crystalline arrangement of the molecules[4]. Degradation of the chains during milling may also be a contributing factor.

Some crystallization is indicated in the patterns of cooled, stretched or unstretched samples of compounded and vulcanized polybutadiene. The sharp ring for the unstretched, and the sharp equatorial arcs for the stretched, material give an interplanar spacing the same as for the distance between chains in pure crystallized polybutadiene. The absence of layer-line spots in the cooled and stretched sample, however, indicate that there is no extended periodicity along the stretch axis.

STRUCTURAL ANALYSIS OF POLYBUTADIENE

Mark[5] states that stretched samples of polybutadiene produced by both mass and emulsion polymerization gave diffraction patterns that indicate a repeat distance of 5.0 Å along the polymer chains. Meyer[6] also mentions this repeat distance. No details are given concerning polymerization temperatures. More recently, Hanson and Halverson[7] obtained diffraction patterns of emulsion and mass (sodium) polymerized butadienes when stretched at low temperatures. They conclude that the emulsion polymer has a repeat distance of about 5 Å, but that the stretched emulsion polymer contains appreciable amounts of oriented noncrystalline material.

To verify this repeat distance of about 5 Å, all of the polybutadiene samples previously described were stretched in the range of 200 to 600 per cent at 0° C, and diffraction patterns were registered on film in a cylindrical cassette to make possible easy measurement of the repeat distance from the layer-line spots. A repeat distance of 5.1 ± 0.1 Å was obtained for samples polymerized at temperatures no higher than 30°. A pattern from a 40° C polymer showed no evidence of layer lines. The layer-line pattern was most pronounced for the −20° polymer, becoming less intense with increasing polymerization tempera-

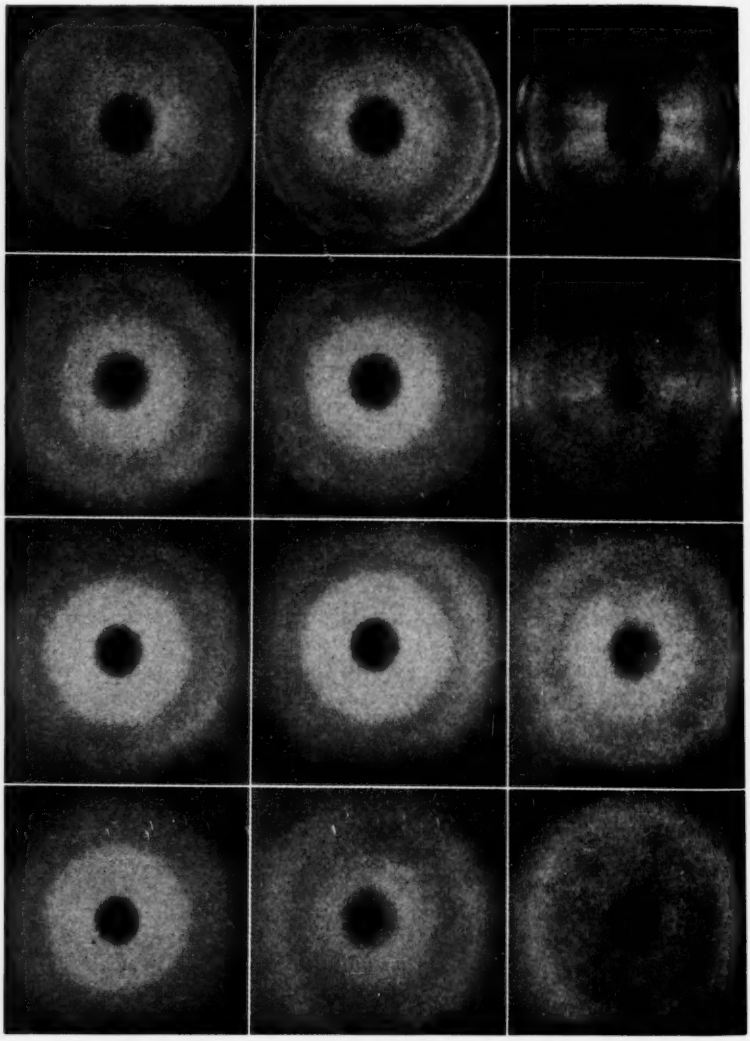
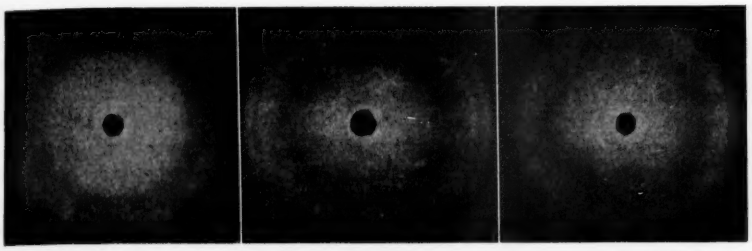
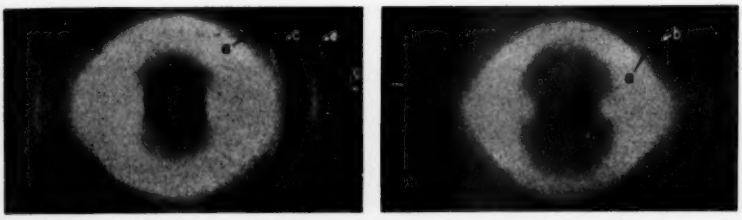


FIG. 6.—Effect of copolymer composition on x-ray diffraction patterns of −20° C polymers (flat cassette patterns).



(*a*) Stretched 400 per cent at 25° exposure at 25° (*b*) Stretched 400 per cent at 25° exposure at −30° (*c*) Unstretched, exposure at −30°

FIG. 7—Flat cassette patterns of compounded −20° C polybutadiene vulcanizate.



(*a*) 300 per cent (*b*) 100 per cent

FIG. 8.—Cylindrical cassette patterns of −20° C polybutadiene at two elongations stretched at 0° C (x-ray exposure at −30° C).

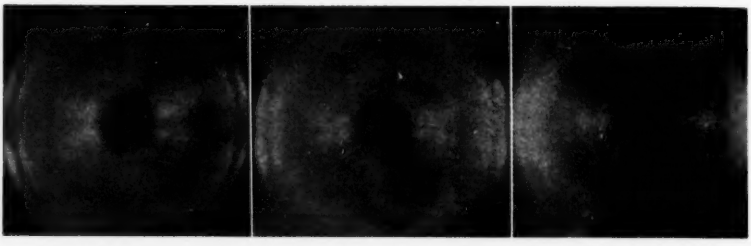
ture and just barely observable for the 30° polymer even with prolonged x-ray exposure. Layer-line patterns obtained from samples of the −20° polymer stretched 300 and 600 per cent respectively, at 0° C are given in Figures 8*a* and 8*b*. The equatorial and first-order layer lines were the only ones that could be registered using unfiltered copper radiation and the particular cylindrical cassette used for this work.

There are two distinct features about the first-order layer line. Spots on at least two diffraction rings near this layer line vary in position with percentage elongation, while spots on three other rings remain fixed in position regardless of the per cent elongation. In Figure 8*a*, at 300 per cent elongation, spots a and b are not on the same layer line, while in 8*b*, at 600 per cent elongation, they are nearly on the same layer line. This phenomenon is summarized in Table III in the columns headed "Behavior of spots in cylindrical cassette patterns". The position marked V (variable) indicate spots that move with percentage elongation. The positions marked F (fixed) indicate that the spots remain in the same position on the ring regardless of the percentage elongation.

The phenomenon of layer-line spots varying in position with percentage elongation was also observed for the diffraction effects obtained in flat cassette patterns of the central diffraction region[8]. A detailed study was made of this effect on the −20° polymer. Preferred orientation became noticeable in the stretched −20° polymer at about 50 per cent elongation. Intense off-equator spots began to appear at about 150 per cent elongation for the diffraction ring having a *d* value of 3.97 Å, and for the inner rings listed in Table III. These off-equator spots moved toward each other with increasing elongation and appeared to coalesce on the equator at about 700 per cent elongation, as shown

in Figure 9. It is interesting to note that, whereas the off-equator spots tend to move toward each other with increasing elongation, the variable layer-line spots move away from each other with increasing elongation.

An effect similar to the coalescence of the off-equator spots is described by Fuller, Frosch, and Pape[9]. They state that 1–16 dicarboxylate polyester (repeat distance of 51.6 Å) gives an x-ray pattern containing intense off-equator spots, these spots coalescing when the polyester is stretched. Their interpretation indicates that the polyester molecules are inclined to the fiber axis and line up parallel to this axis when the polyester is stretched. The same hypothesis would reasonably explain why the off-equator spots observed in the present work move toward the equator with increasing elongation. On this basis, the maximum inclination of the molecules to the stretch axis, as measured by the angle the off-equator spots make with the equator, was found to be about 20°. Further work is necessary to establish whether or not the motion of the first-order layer-line spots is fully consistent with the above picture.



300 per cent 500 per cent 700 per cent

FIG. 9.—Flat cassette patterns of −20° C polybutadiene at three elongations stretched at 0° C (x-ray exposure at −30° C).

The repeat distance of 5.1 Å corresponds quite closely to the length (5.05 Å) of a fully extended planar butadiene unit with normal bond angles and lengths. The fact that there is only one butadiene unit per repeating unit in the polymer chain indicates also that the chains in the crystalline portion of the polymer are in the *trans*-configuration. The *cis*-configuration would require at least two butadiene units to complete a single geometrical repeating unit.

By properly cooling and stretching the −20° C polymer, the amorphous halo present at room tempeature can be made to disappear nearly completely, and the intensity of the diffraction spots reaches a maximum. Under these conditions the major portion of the polymer is undoubtedly crystalline, indicating that most of the double bonds are in the *trans*-configuration. However, the purified polymers contain about 14 per cent of vinyl groups (resulting from 1,2-addition) that are presumably distributed at random along the chains. These groups probably are not included in the crystalline regions, since they would prevent periodicity in the structure. Their presence, therefore, limits the amount of polymer that can crystallize.

SYNOPSIS

The fine structures of emulsion polybutadiene prepared at temperatures ranging from 55° to −20° C and of various butadiene-styrene copolymers prepared at −20° C have been studied by x-ray methods. The ability of emulsion-polymerized butadiene to crystallize was found to depend to a large extent

on the temperature of polymerization. Butadiene polymerized at 30° C and above showed no evidences of crystallization when cooled unstretched to −70° C, as observed by x-ray diffraction methods; however, butadiene polymerized at 20° C and below showed crystallization effects when cooled unstretched to −70° C. These crystallization effects became more pronounced for samples polymerized at lower temperatures. Layer-line diffraction patterns of butadiene polymerized at 30° C and below were obtained by stretching the polymer at about 0° C. From these patterns the geometrical repeat distance along the polymer chains was found to be 5.1 ± 0.1 Å. This corresponds to a fully extended butadiene unit in the *trans*-configuration. An anomaly was observed in the diffraction patterns of crystallizable polybutadiene stretched at 0° C. Some of the layer-line spots varied in position with percentage elongation of the sample. This suggests that the molecules in crystallites of the polymer are inclined to the stretch axis at low elongations and that they become more nearly parallel to the stretch axis at higher elongations. A small addition of styrene as comonomer at −20° C polymerization temperature did not prevent crystallization and preferred orientation effects in the polymer, since these effects could still be found in a 90/10 charge copolymer. Larger amounts of styrene did prevent crystallinity and preferred orientation as shown by the amorphous nature of an 80/20 charge copolymer. The ability of a compounded vulcanizate of a given polymer to crystallize is less than that of the purified polymer under the same conditions. This may be due to the combined effects of milling, vulcanization, and the presence of carbon black particles in the polymer. A description of the apparatus and techniques used for cooling and stretching these polymers is given.

ACKNOWLEDGMENT

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INFLUENCE OF STRUCTURE ON POLYMER–LIQUID INTERACTION. III. SWELLING AND MECHANICAL PROPERTIES OF SOME PARTLY CRYSTALLIZED POLYMERS *

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We have shown in the first part of this work[1] the influence of association on liquid–polymer equilibrium, while a study of nitrile copolymers[2] revealed that mechanical properties are much more sensitive to certain changes in polymer structure (such as the introduction of methyl groups) than are swelling equilibria. In partly crystallized polymers, however, a close correlation between liquid–polymer interaction and mechanical properties exists, as is seen from the present paper.

GUTTA-PERCHA AND NATURAL RUBBER

It is known that the outstanding difference between raw gutta-percha and raw rubber is in the tremendous rate of crystallization of the former. It becomes evident not only on cooling the solid polymer below its melting point but also in the following two groups of precipitation experiments.

(1) A 1 per cent solution of the polymer in toluene was prepared and the precipitating power of a number of polar liquids was tested by measuring the point of first turbidity. Results for natural rubber are compiled in Table VIII of Part I. Since the molecular weight of gutta-percha is lower than that of rubber[3], one should expect the former to be more soluble than the latter. However, the reverse is actually true: the volume fraction of the nonsolvent at the precipitation point is always about 10 per cent smaller than that for rubber. Under these conditions, methylpropyl ketone is a solvent for rubber but a precipitant for gutta-percha. The gel phase immediately exhibits syneresis due to the beginning of crystallization.

(2) A 1–3 per cent solution of gutta-percha in hexane was prepared and mixed above room temperature with a 1–3 per cent solution of rubber in the same solvent. On cooling to 0° C, the gutta-percha fraction crystallized out completely, even in the presence of 5–9 times its weight of rubber. The general tendency of polymer mixtures to separate[4] becomes prevalent even in a mixture of these two isomers. The theoretical explanation given by Gee[5] can be applied to the equilibrium finally reached in these experiments: on mixing rubber and gutta-percha the gain in entropy of mixing is very small, and is therefore insufficient to compensate for the heat of crystallization of gutta-percha.

The degree of swelling of gutta-percha differs also from that of rubber (see Table I).

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The influence of crystallinity, which becomes evident from Table I, can be readily understood from a comparison with the behavior of two other partly crystalline polymers—polythene[6] and cellulose[7]. The melting point of polythene is lowered by the presence of a solvent, the degree of depression depending on the nature and concentration of the liquid. The same is true for gutta-percha. Benzene depresses the melting point below room temperature, while hexane and pentane dissolve only a part of the crystals and act as swelling agents on the amorphous phase. This degree of swelling depends on experimental conditions, as can be deduced from the behavior of vulcanized gutta-percha (see below). On the other hand, the interaction of ketones with polythene or crystalline gutta-percha is very weak and the liquids are taken up only in the amorphous regions. The latter phenomenon is quite comparable to the swelling of cellulose. The influence of crystallinity on mechanical properties and on swelling equilibria will now be deduced from a study of vulcanized samples.

TABLE I

SWELLING OF RAW RUBBER AND GUTTA-PERCHA AT 20° C IN MOLAR FRACTIONS

Solvent	Benzene	Hexane	Pentane	Pentanone	Butanone	Acetone
Rubber	1	1	1	0.75	0.36	0.14
Gutta-percha	1	0.31	0.31	0.10	0.10	0.07

The vulcanization of natural rubber is accompanied by a reduction of the crystalline phase formed on stretching (compared with the same quantity in extended raw rubber). The correlation between the percentage of sulfur chemically bound to the rubber molecule and the amount of this crystalline phase at low temperature is used as a direct measure of the degree of vulcanization (T-50 test)[8]. One can, therefore, expect sulfur vulcanization also to reduce the proportion of crystalline phase in gutta-percha. In fact, van Rossem and Soudijn[9], studying mixtures of 100 parts gutta-percha and 8 parts sulfur, succeeded in producing a rubber from gutta-percha after sufficiently long vulcanization times. Dawson, Johnson, and Scott[10], on the other hand, in their investigation of accelerated mixtures with only 5 parts sulfur, found stress–strain properties quite similar to those described by Parks[11] and still very different from those of a rubber. We have made use of a low-sulfur accelerated pure-gum stock to achieve the advantage of cross-linking and still to minimize the influence of sulfur. The stress-strain properties are summarized in Figure 1. The first 15 minutes of vulcanization reduces the yield point considerably, but the shape of the curve still resembles that of the raw polymer. A further increase in vulcanization time by a factor of ten has comparatively little influence on the yield point, but the slope of the stress–strain curve after flow has set in finally resembles that of rubber. Figure 1 suggests, therefore, that the main decrease in crystallinity occurs within the first 15 minutes of vulcanization; this can be corroborated by the following observations.

(1) The specific gravity, which normally increases on vulcanization of natural rubber, decreases on vulcanization of gutta-percha by 0.008 after 15 minutes.

(2) A strip of raw gutta-percha stretched 200 per cent for 24 hours at 50° C shows little recovery one hour after release of the tension. With a vulcanization time of 15 minutes, about 30 per cent recovery has been measured: 30-

minute vulcanization gives 80 per cent; and 45–150-minute vulcanization gives nearly complete recovery at 50° after one hour. This improvement in elasticity can be followed equally well by immersing the stretched strips in a 50 per cent benzene–alcohol mixture at 20°; strips vulcanized for 30 minutes recover readily.

(3) Still another method of following the same phenomenon is analogous to the T-50 test. The limiting temperature for preponderantly elastic behavior is 60° C for a strip of gutta vulcanized for 15 minutes, and 50° for strips vulcanized for longer periods of time; but no further decrease in elasticity temperature has been observed, a result which is in good agreement with Figure 1. This phenomenon—the occurrence of a limiting temperature of elasticity—is clearly caused by the formation of crystals below ±50°. It is indicated also by a sudden decrease in the solubility and diffusivity of gases in vulcanized gutta-percha between 45° and 50° [12].

We have found (Figure 2) that the degree of cross-linking after 45-minute vulcanization, as indicated by the amount of swelling in chloroform, benzene, and cyclohexane, is identical with that of rubber after the same vulcanization time. The swelling in pentane reaches the value for rubber only gradually, while the influence of vulcanization is much more pronounced in hexane. From a comparison of Figures 1 and 2 it becomes evident that the mechanical properties are again much more sensitive to changes in crystallinity than the swelling equilibrium.

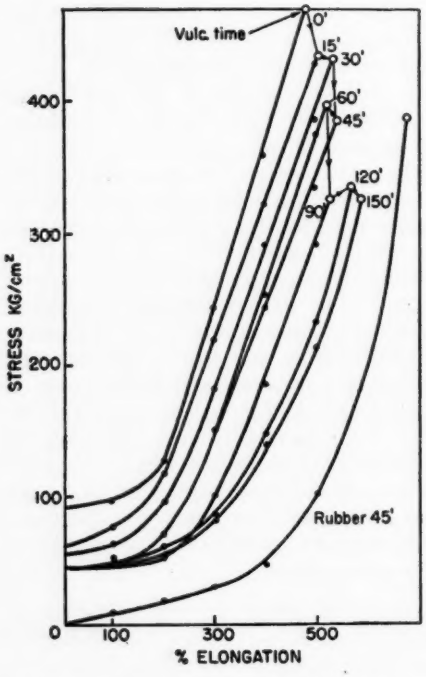

FIG. 1.—Stress-strain properties of vulcanized gutta-percha. Mixture: gutta-percha 100 (purity 98.5 per cent; resin 1.5 per cent), sulfur 2, Zimate 1, zinc stearate 3, Age-Rite White 1; vulcanization temperature 120° C.

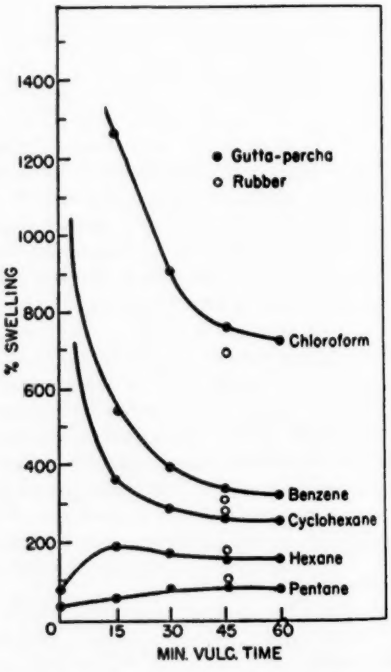

FIG. 2.—Influence of vulcanization on degree of swelling of gutta-percha at 20° C (see Figure 1 for mixture).

Vulcanization leads not only to a reduction in crystallinity but also to a typical dependence of (apparent) swelling equilibria and rate of recrystallization on the prior history of the sample. The 15-minute sample immersed at 0° C in hexane swells only to about 20 per cent (Figure 3 *A*); on warming to 25° swelling increases to 150 per cent; but on cooling again recrystallization is incomplete and the degree of swelling is therefore higher. The same phenomenon has been observed starting from 25° and cooling to 0° (Figure 3 *B*). In the third experiment (Figure 3 *C*), swelling equilibrium was first established at 50° C; no crystallization at all could be produced on cooling the strongly swollen sample to 25°, and only little crystallization occurs at 0°.

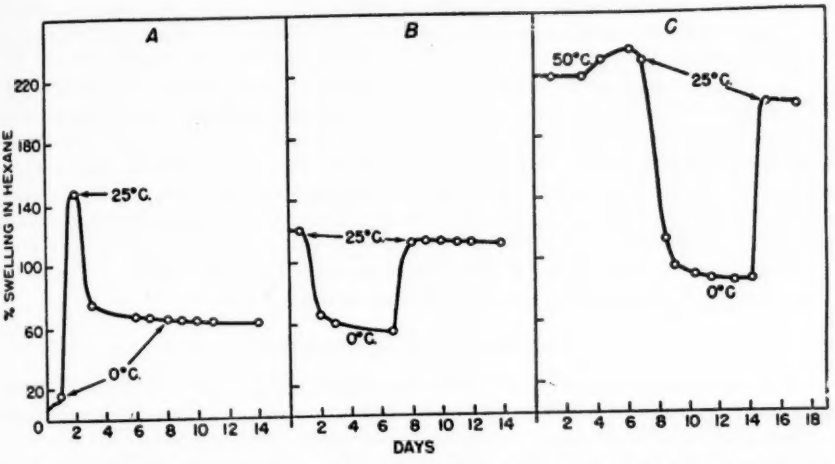

FIG. 3.—Influence of temperature on degree of swelling. Gutta-percha vulcanized 15 minutes. *A*, equilibrium at 0° C, gel warmed up to 25°, and new apparent equilibrium at 0°; *B*, equilibrium at 25°, cooled to 0° and recovery of the first equilibrium at 25°; and *C*, equilibrium at 50° and apparent equilibrium at 25°, 0° and again 25°.

Figure 3 suggests a formal analogy between the crystallization of swollen vulcanized gutta-percha and raw rubber. The melting point of the latter depends on the previous history of the sample[13]. From density and x-ray measurements[14] it has become clear thst the amount of crystalline phase increases with an increase in melting point. Crystallization in raw rubber is induced by local strains caused by the method of handling and storing the material. It corresponds actually to the process of crystallization in a slightly extended rubber, in which the amount of crystalline phase, as well as the melting point, depends on the degree of stress. Rubber crystallized from ether solution at −60° C melts always at or below +11° [15]. It is fairly safe to predict that the amount of crystalline phase in these "crystals" will be found to be only about 15 to 20 per cent. Turning back now to Figure 3, the probable theoretical explanation of the phenomenon is as follows. The presence of crystals in the partly swollen gel causes a certain degree of orientation in the amorphous chain sectors, facilitating further recrystallization. In completely swollen vulcanized gutta-percha the free rotation of chain segments is hampered and nucleus formation more difficult than from a solution of raw gutta-percha. The rate of crystallization even at 0° is therefore low.

The amount of crystallized phase in raw rubber is much smaller than that in

raw gutta-percha[13]. For this reason it is not possible to observe the limited swelling of partly crystallized rubber in hexane as with the behavior of gutta-percha. Obviously the gain in entropy on dissolution compensates for the heat of crystallization and, as a consequence, crystallized rubber dissolves even at 0° C. The quantity of crystalline phase can be increased by a process of repeated orientation termed racking[1]. Feuchter[17] has claimed that strips of racked rubber are "nonswelling" in gasoline. We cannot confirm these observations. Racked rubber, originally extended 700–4000 per cent, contracts within 3–4 minutes when immersed in hexane and is strongly swollen after that time. If a strip is fixed in the extended position and then allowed to swell, absorption of liquid starts perpendicularly to the direction of stress; the strip becomes weak and breaks after a short time. Feuchter's experiments therefore refer to a kinetic phenomenon (actually the rate of swelling is reduced by orientation of the rubber chains), but not to a state of equilibrium. We finally succeeded in vulcanizing racked rubber by immersion for 10 seconds in a 3 per cent solution of sulfur chloride in carbon disulfide. Such strips were apparently unchanged, but swelling in benzene and chloroform revealed that they were cross-linked. Attempts to reproduce the "nonswelling" of Feuchter with such strips also failed completely. Racked rubber must contain more crystalline phase than raw gutta-percha, and the entropy of mixing alone is not therefore sufficient to compensate for the heat of crystallization, but an additional contribution is made by the gain in entropy on contracting. The latter term obviously determines the solubility of extended rubber.

RUBBER HYDROCHLORIDES

The position of rubber hydrochlorides within a family of polymers has been discussed in another paper[18]. The outstanding property of these hydrochlorides is their ease of crystallization from solutions, quite comparable to that of gutta-percha and the great stability of these crystals, which can survive even in a swollen state[19].

We have prepared hydrochlorides from vulcanized rubber by applying the following method. A low sulfur mix, omitting zinc oxide, was used (100 deproteinized crepe, 2 sulfur, 1 Zimate, 3 zinc stearate, 1 Age-Rite, vulcanized 15 minutes at 120° C). Plates of 1-mm. thickness were swollen in ethyl acetate and reacted with a saturated solution of hydrochloric acid in ethyl acetate. The mechanical properties and the degree of swelling are compared in Figure 4.

Elongation at break (Figure 4 *A*) is not much changed by hydrochlorination, but after 25 per cent reaction has taken place the vulcanized sample becomes very weak (Figure 4 *B*), comparable to a noncrystallizing elastomer. Suddenly, after about 60 per cent of the available double bonds have been hydrochlorinated, the samples exhibit a very high tensile strength at break. Simultaneously the rate of elastic recovery becomes very small (Figure 4 *C*), comparable to the behavior of vulcanized gutta-percha. The swelling properties of these vulcanizates (Figure 4 *D*) change little in benzene (curve 1), but show a sudden decrease in hexane (curve 2) as soon as partial crystallization becomes evident in mechanical tests. Hardening caused by continuously increasing crystallization is reflected also in a further reduction of the swelling in hexane (curves A and B in Figure 4 *D*). Summing up the changes by hydrochlorination (Figure 4) indicates: (1) a limiting chlorine concentration (±20 per cent Cl) for crystallization on stretching, combined with a loss of elastic recovery, and (2) a gradually increasing tendency of the unstretched samples to crystallize.

We have found that the corresponding hydrochloride from gutta-percha is also partly crystallized, and exhibits the same x-ray pattern as the product made from rubber[20]. The mechanical properties of films made from gutta-percha hydrochloride suggest the presence of a smaller crystalline fraction, and this may explain earlier statements of an apparently amorphous structure. The hydrobromides of rubber and gutta-percha also contain a crystallized fraction[20]. Their x-ray patterns are very similar to, or identical with, those of the hydrochlorides, indicating that chlorine and bromine are exchangeable in these unit cells; this is already known from a comparison of bromoprene and chloroprene polymers[21]. The fact that these hydrobromides contain a crystalline fraction does not necessarily mean that they consist only of tertiary bromide; in fact, kinetic studies still in progress indicate the simultaneous formation of the secondary bromide.

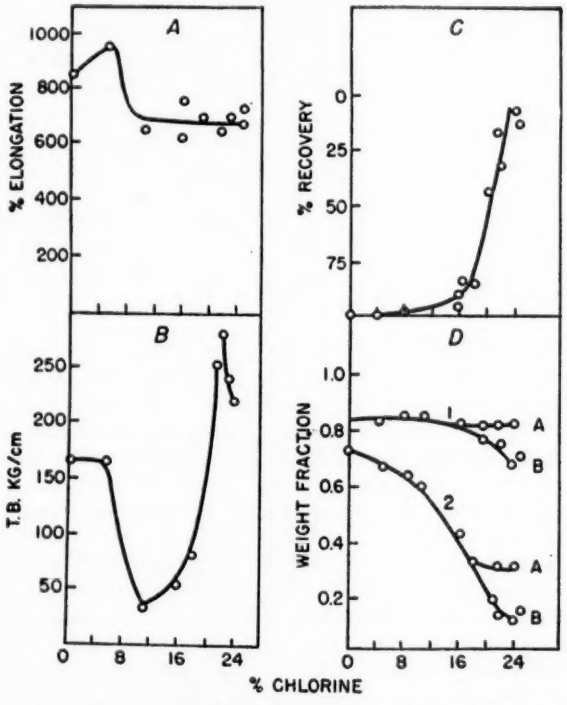

FIG. 4.—Influence of chlorine concentration on mechanical properties and swelling of vulcanized rubber hydrochlorides. *A*, elongation at break; *B*, tensile strength at break (calculated on original cross-section); *C*, elastic recovery at 20° C (strip extended 200 per cent for 24 hours); and *D*, swelling equilibria (calculated as weight fraction) in benzene (curve 1) and hexane (curve 2) measured on fresh samples (curve 1*A* and 2*A*) and on samples shelf-aged for 1 month (curves 1*B* and 2*B*).

DISCUSSION OF RESULTS

Gutta-percha and rubber hydrochlorides have a number of properties in common. They crystallize readily from solutions and from the amorphous polymer. The mechanical properties depend greatly on the degree of crystallinity, as is generally the case in partly crystalline polymers. Although quantitative measurements are still lacking, the impression is gained that the melting

of crystals in a stretched sample under the influence of contraction—a property so typical for natural rubber—occurs to a minor degree only in these partly crystallized polymers.

This would mean that the gain of configurational entropy on contraction is larger for rubber than for gutta-percha. One could surmise from this a correlation between the shape of molecules in solution and ease of crystallization. Although experimental evidence is still too scanty for a general theory, the following division of partly crystalline polymers can be made[18].

Group I.—Polymers that crystallize readily from solution and(or) from the molten amorphous phase: Teflon, polythene, polyvinylidene chloride, rubber hydrochloride, gutta-percha. The first two are very symmetrical, and a high rate of crystallization could be expected. This is not the case with the other three polymers, and one cannot do much more at present than sum up the obvious elements of symmetry essential for the formation of crystals; these factors are not sufficiently understood to predict the high rate of crystallization. In polyvinylidene chloride a symmetrical energy distribution exists at the CCl_2 group, and this may contribute to its superior rate of crystallization in comparison to polyvinyl chloride. Rubber hydrochloride, on the other hand, has only a symmetrical chain axis, and the additional assumption has been introduced that either the *d* or the *l* form is preponderant[22]. The impression is gained from the space model of gutta-percha that the crystal lattice is more easily formed than in rubber; while this may contribute to the rate of crystallization, it does not explain the higher melting point of the crystals. It seems possible that the gain of configurational entropy in the process of melting or dissolving gutta-percha is smaller than in the case of rubber, *i.e.*, that the gutta-percha chains in the amorphous and dissolved states are less flexible than those of rubber.

Group II.—Comprises plastics that do not crystallize from solution and only difficultly from the amorphous polymer. Crystallization may be enhanced by the presence of plasticizers or by stretching. The main representatives of this class are vinyl derivatives, such as: polyvinyl fluoride, polyvinyl alcohol, polyacrylic nitrile, and polyvinyl chloride. Following the line of thought developed by Bunn[23] we must assume that the size of the substituent is decisive for determining the ease of crystallization, the uneven charge distribution together with the occurrence of mixed *d* and *l* forms making the chain irregular. The heat of crystallization is insufficient to compensate for the loss of configurational entropy that would be caused by crystallization from solution. Under the influence of external forces on stretching, this entropy factor is compensated for, and crystallization occurs. On stretching and in solution, therefore, these polymers behave comparably to the third group.

Group III.—This group is made up of the true elastomers—natural rubber, Neoprene, and Butyl rubber—which combine a slow rate of crystallization in the unstretched state with an instantaneous crystallization on stretching. Here, the entropy gain on contracting compensates for the heat of melting, a factor essential for the rubberlike state.

Neither Butyl rubber nor Neoprene exhibits the typical dependence of the melting point on the degree of stress which is so well known for natural rubber. In the case of Neoprene this is probably due to a lack of regularity in the Neoprene chain. Sutherland[24] has recently proved by infrared measurements that Neoprene is (*a*) a straight chain 1,4-addition polymer, but (*b*) of *cis* and *trans* groups. The latter conclusion is supported by the incomplete addition of ICl and Br_2 to the double bond in Neoprene[25]. In analogy with gutta-percha, we

can assume that the *trans* groups in Neoprene crystallize readily. In fact, it is well known to workers in this field that vulcanized Neoprene crystallizes readily at about 0° C on storing. The amount of crystalline fraction in Neoprene is not yet known, but, in contrast to the behavior of natural rubber, further crystallization is inhibited by the presence of *cis* groups. This explains why natural rubber crystals exist even at 100° C, whereas those of extended Neoprene melt readily even at moderate temperatures[1].

The transformation of natural rubber into the crystalline complex compound with silver nitrate occurs in the swollen state with great ease[18]. This formation of π bonds[25] leads to a reduction in chain mobility and illustrates the gradual change from Group III to Group I.

SYNOPSIS

Swelling and rate of crystallization from solution and gels of raw and vulcanized gutta-percha have been studied. Sulfur vulcanization of gutta-percha causes a reduction in the proportion of crystalline phase that becomes evident from typical changes in mechanical and swelling properties. Liquid–polymer interaction of the crystalline phase in gutta-percha, raw rubber, and racked rubber lead to different equilibria, which are probably due to differences in the free energy contents of the crystalline phases. A series of vulcanized rubber hydrochlorides with gradually increasing chlorine content show analogous changes in rate of elastic recovery and swelling equilibria that are also due to the gradual formation of a crystalline phase. Correlations between molecular structure and rate of crystallization in plastics and elastomers are discussed. Symmetry of the shape, as well as of intermolecular forces in the molecular units, size of substituents, and regularity of the polymer chain all have an essential influence on the rate and ease of crystallization.

ACKNOWLEDGMENT

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REFERENCES

[1] Salomon and Van Amerongen, *J. Polymer Sci.* **2**, 355 (1947); RUBBER CHEM. TECH. **21**, 66 (1948).
[2] Salomon, *J. Polymer Sci.* **3**, 173 (1948); RUBBER CHEM. TECH. **21**, 805 (1948).
[3] Wolff, *Helv. Chim. Acta* **23**, 439 (1940).
[4] Dobry and Boyer-Kawenoki, *J. Polymer Sci.* **2**, 90 (1947).
[5] Gee, *Quart. Revs.* **1**, 290 (1947).
[6] Richards, *Trans. Faraday Soc.* **42**, 10 (1946).
[7] Hermans, "Contribution to the Physics of Cellulose Fibers", Elsevier, New York-Amsterdam, **1946**, p. 52.
[8] Vila, *India-Rubber World* **101**, 34 (1939).
[9] Van Rossem and Soudijn, *Gummi-Ztg.* **52**, 1070 (1938).
[10] Dawson, Johnson, and Scott, *J. Rubber Research* **15**, 26 (1946).
[11] Parks, *Ind. Eng. Chem.* **17**, 172 (1925).
[12] Van Amerongen, *J. Polymer Sci.* **2**, 381 (1947).
[13] Van Rossem and Lotichius, *Kautschuk* **5**, 2 (1929).
[14] Goppel, J. M., Thesis, Delft, **1946**.
[15] Smith, Saylor, and Wing, *Bur. Standards J. Research* **10**, 479 (1933); Smith and Saylor, *Bur. Standards J. Research* **13**, 453 (1934).
[16] Whitby, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, New York, **1937**, p. 70.
[17] Feuchter, *Kautschuk* **2**, 176 (1926).
[18] Salomon and Koningsberger, *J. Polymer Sci.* **2**, 522 (1947).
[19] Gehman, Field, and Dinsmore, *Proc. Rubber Tech. Conf. London*, **1938**, p. 968.
[20] Arlman, J. J., private communication.
[21] Carothers, *Ind. Eng. Chem.* **26**, 30 (1934).
[22] Bunn and Garner, *J. Chem. Soc.* **1942**, p. 654.
[23] Bunn and Peiser, *Nature* **159**, 161 (1947).
[24] Sutherland, in "The Labile Molecule. A general discussion", *Trans. Faraday Soc.* **43** (1947).
[25] Salomon, in "The Labile Molecule. A general discussion", Trans. Faraday Soc. **43** (1947).

REACTION KINETICS OF ADIABATIC SYSTEMS *

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LIST OF SYMBOLS

T	Temperature (° K)
k_n	Mass law constant of order n
t	Time (min.)
n	Order of reaction
X	Pre-exponential frequency factor in Arrhenius Law
C	Average specific heat of system (cal. ° K^{-1} $kg.^{-1}$)
c	Molality (mol. $kg.^{-1}$)
H	Heat of reaction (cal. $mol.^{-1}$)
E	Apparent energy of activation (cal. $mol.^{-1}$)
Q	$E/R(1/T - 1/T_f)$
M	Maximum slope dT/dt of heating curve

Subscripts and Superscripts

Subscript 0	Refers to zero time
Subscript f	Refers to final, or asymptotically approached, values
Star (T^*)	Refers to temperature where d^2T/dt^2 vanishes
Dash (T')	Refers to temperature where d^3T/dt^3 vanishes (provided $T' < T^*$)
Double Dash (T'')	Refers to temperature where d^3T/dt^3 vanishes (provided $T'' > T^*$)

Kinetic measurements are conventionally carried out at constant temperature and expressed in terms of velocity constants k_n, calculated from the law of mass action. From a series of runs at different temperatures, the well-known Arrhenius plot leads to the determination of E and X. According to the new method here proposed, reaction runs are carried out adiabatically instead of isothermally. There are both advantages and disadvantages attached to this change. The mathematical treatment is necessarily more complicated when an additional parameter, temperature, is allowed to vary instead of being kept constant; on the other hand, the temperature change becomes available as a physical property for following the progress of a reaction, and puts the accuracy of modern thermometric equipment at the disposal of the kineticist. Before weighing such factors in a critical discussion, the mathematical evaluation of kinetic time-temperature data will be described.

When a reaction proceeds adiabatically, the temperature varies with time, owing to the reaction heat liberated or consumed, and one obtains socalled heating or cooling curves. The differential equation appropriate to such curves will first be deduced on the basis of six assumptions; next the evaluation of the parameters n, E and X from certain plots based on this equation is

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explained. Such plots are founded on the data of a single adiabatic run, though a special technique, compounding data from a number of runs, will also be mentioned. Moreover, the differential equation may be differentiated to obtain relations involving special points which can be spotted on a heating curve, especially the inflection point; these points and relations are valuable, since they give immediate estimates of n and E.

Finally the differential equation can be solved if n and E are known and n is integral. We thus obtain a direct and complete check by comparing experimental and theoretical time-temperature curves, since the theoretical law, in its integrated form, permits the quantitative prediction of the complete heat effect of a chemical reaction carried out adiabatically. Data are already extant on the heat effect of reactions used technologically, particularly in the polymer field and, within the limits of the listed assumptions, this paper provides the mathematical theory underlying such data.

Assumptions.—(1) The law of mass action holds.

Activity coefficients are assumed to be equal to unity. Weight concentrations replace the conventional volume concentrations, both for convenience and to make some allowance for volume changes, if any, occasioned by the reaction progress and/or the change in temperature[1]. Except where the contrary is stated, the mass concentrations of all reactants which significantly diminish (by reacting away) are taken to be molecularly equivalent.

(2) The law of Arrhenius relating velocity constants with temperature holds.

(3) The heat change is due practically exclusively to a single reaction. In particular this requires that (*a*) secondary chemical or physical changes do not contribute thermal effects to the heating or cooling curve, and (*b*) secondary changes do not enter into the kinetics of the main reaction. Thus the reacting or catalyzing species of the main reaction are neither produced nor consumed significantly in secondary chemical changes, whether these be relatively slow, so as to enter the kinetic scheme as rate constants, or fast enough to enter it as equilibrium constants.

(4) The heat of reaction is independent of temperature.

(5) The specific heat of the system is independent of temperature and composition.

(6) The system is sufficiently closely adiabatic.

MATHEMATICAL ANALYSIS OF ADIABATIC HEATING AND COOLING CURVES

The fundamental law governing the time-temperature plot of an adiabatic reaction is deduced as follows. Assumptions (4) to (6), and the last part of assumption (1), together imply that the rate of temperature change is a direct measure of the progress of an adiabatic reaction. Thus:

$$|T_f - T| = cH/C \tag{1}$$

or in differential form:

$$\pm \mathrm{d}T = (H)C\mathrm{d}c \tag{2}$$

Next, combining the mass law for a nth order reaction:

$$k_n = -c^{-n}\mathrm{d}c/\mathrm{d}t \tag{3}$$

with the Arrhenius law:

$$k_n = X\mathrm{e}^{-E/RT} \tag{4}$$

we obtain by eliminating k_n:

$$dc/dt = - Xc^n e^{-E/RT} \tag{5}$$

In this equation we finally eliminate the concentration c by substituting from Equations (1) and (2):

$$\pm dT/dt = X(C/H)^{n-1}(T_f - T)^n e^{-E/RT} \tag{6}$$

and thus obtain the fundamental differential equation governing the heating or cooling curves of adiabatic reactions.

A slight rearrangement gives a form convenient for plotting experimental data. For all but first-order reactions we have:

$$n \neq 1: \qquad \ln [d(T_f - T)^{1-n}/dt] = \ln [(n-1) \cdot X \cdot (C/H)^{n-1}] - E/RT \tag{7}$$

while for a first-order reaction Equation (8) holds:

$$n = 1: \qquad \ln [- d \ln (T_f - T)/dt] = \ln X - E/RT \tag{8}$$

In either case the left-hand side—obtained from experimental data—is plotted against $1/T$, and E found from the slope. If n is correctly chosen, a straight-line plot is obtained in all cases. The important first-order case is fortunately independent of H and C, and X is directly obtained from the intercept. When $n \neq 1$, the calculation of X requires an estimate of the ratio C/H which will generally be obtained by substituting the initial experimental values T_0 and c_0 in Equation (1), though independent measurements could be used.

Turning now to the general outline of curves obeying the differential law of Equation (6), it is clear that in endothermic reactions $T > T_f$ and dT/dt is negative, increasing steadily to zero, its asymptotic value. The much larger class of exothermic reactions now to be discussed lead to the **S**-shaped heating curves familiar in thermal studies of vulcanization, polymerization, etc. According to Equation (6), the **S**-shape results from the progressive balancing and final swamping of the temperature effect (exponential term) by the mass action effect represented by the term $(T_f - T)^n$. Formally any exothermal adiabatic reaction obeying Equation (6) belongs to an **S**-shaped heating curve, which may be extrapolated in theory back to an asymptotic approach of the absolute zero. This feature is shown in the accompanying sketch, which also illustrates results obtained by forming the first two differential coefficients of Equation (6) with respect to time. The vanishing of the first locates the inflection point of the **S**-shape:

$$T_f - T^* = nRT^{*2}/E \tag{9}$$

The vanishing of the second locates the points T' and T'':

$$T_f - T' = G'nRT'^2/E \tag{10}$$

$$T_f - T'' = G''nRT''^2/E \tag{11}$$

where G' and G'' are easily calculated functions of n (and, formally, of the ratios E/T' and E/T'' respectively; the slight dependence of G' and G'' on these ratios can be neglected).

A spotting of these points—particularly the easily found inflection-point—saves unnecessary graphing by suggesting the correct value of n; thus two heating curves agreeing in all their parameters except that one belongs to a first-

the other to a second-order, reaction, have in practice inflection points 15° or 20° apart. Moreover, the temperature being measured electrically, and since currents can be differentiated with respect to time quite accurately by well-known electrical circuits, direct measurement of these critical points by electrical null methods does not seem excluded; hence E and n would be found and checked from Equations (9) to (11).

Instead of confining attention to a single heating curve, one can combine data from a number of adiabatic runs on the same reaction. Thus a linear plot can be based on measurements of T^* and the slope M at T^* (see Figure 1) for a number of runs according to the following equation:

$$\ln M^{1/n}/T^{*2} = -E/nRT^* + \ln (nR/E) + (1/n) \ln X + [(n-1)/n] \ln (C/H) \quad (12)$$

The left-hand side is plotted against $1/T^*$.

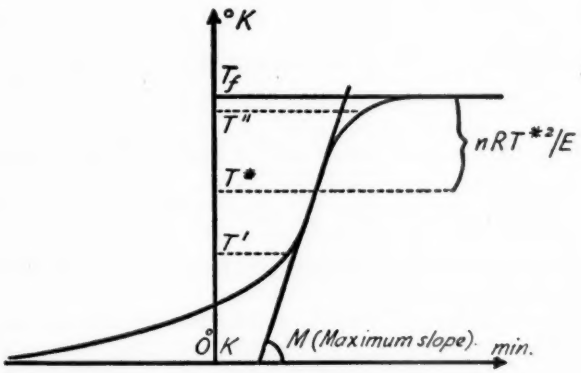

FIG. 1.—Sketch of typical heating curve.

While a number of ways have now been presented for working up mathematically time-temperature data of adiabatic reactions, a direct comparison between theory and practice, as distinct from a mere computation of the best parameters to fit given curves, is afforded only by direct solution of the differential Equation (6).

INTEGRATION OF THE ADIABATIC HEATING AND COOLING LAW

For integral reaction orders n, Equation (6) can be integrated in terms of the tabulated exponential integral:

$$E_i(y) = \int_{-\infty}^{y} (e^x/x)dx \quad (13)$$

One uses the substitution:

$$Q = (E/R)(1/T - 1/T_f)$$

so that:

$$T_f - T = RT_f^2Q/(RT_fQ + E)$$

and

$$T = ET_f/(RT_fQ + E) \quad (14)$$

in Equation (6) and obtains:

$$\frac{dt}{dQ} = \frac{dt}{dT} \cdot \frac{dT}{d(1/T)} \cdot \frac{d(1/T)}{dQ}$$

$$= -\frac{1}{X}\left(\frac{C}{H}\right)^{1-n}\left(\frac{RT_fQ + E}{RT_f^2Q}\right)^n e^{E/RT_f}e^Q \cdot \left(\frac{ET_f}{RT_fQ + E}\right)^2 \cdot \frac{R}{E} \quad (15)$$

Hence:

$$t = \alpha \int \frac{(RT_fQ + E)^{n-2}}{Q^n} e^Q dQ \quad (16)$$

(with the proper limits of integration) where α is a known quantity.

The last integral is expressed in terms of the subsidiary integrals:

$$J_r = \int e^Q/Q^r dQ \qquad \text{with} \qquad 2 \leqslant r \leqslant n \quad (17)$$

J_r is itself reduced to $J_1 = E_i(Q)$ by integration by parts thus:

$$(r - 1)J_r = J_{r-1} - e^Q/Q^{r-1}, \text{ etc.} \quad (18)$$

The unimolecular case, $n = 1$, can be easily integrated, the solution being:

$$t = \pm \frac{1}{X}\left[E_i\left(\frac{E}{RT}\right) - E_i\left(\frac{E}{RT_0}\right) + e^{E/RT_f}[E_i(Q_0) - E_i(Q)] \right] \quad (19)$$

where the positive sign on the right-hand side refers to an exothermic, the negative to an endothermic reaction.

It should be noted that X generally enters the solutions merely as a multiplier of t; variations in its value are therefore equivalent to a variation in the time unit employed. It is, accordingly, sufficient to know n and E to compare an experimental heating or cooling curve with its correct theoretical counterpart. These theoretical curves, typified by Equation (19), form the basis of interpretation of time-temperature data collected by chemical technologists investigating the heat-effect of reactions carried out adiabatically.

DISCUSSION

We now come to a discussion—of a preliminary nature—of the possible value of the adiabatic method for making kinetic measurements. A full statement will clearly have to await the execution of planned adiabatic experiments on reactions selected from the wide range already explored by the isothermal technique.

When examining the validity of the listed assumptions on which our mathematical treatment is based, two general considerations are of importance. The first is that assumptions (4), (5) and (6), and usually (2) and (3) also, are true limiting conditions as the range of time-temperature measurements considered is reduced. This is also true of deviations from molecular equivalence as postulated in assumption (1). While it is obvious that in practice a reduction in the range of data employed is sooner or later checked by the attainable accuracy of thermal measurements, a brief note on modern thermometric technique will show that measurements can in fact be made accurately on relatively narrow ranges.

The second consideration is founded on the fact, according to Equations (7)

and (8), the adiabatic plots are analogous in form to the traditional Arrhenius plots, the expressions $\ln [d(T_f - T)^{1-n}/dt]$ and $\ln [-d \ln (T_f - T)/dt]$ taking the place of k_n and k_1, respectively. If these expressions can, therefore, be measured as accurately as the traditional mass law constants, the same temperature ranges as are normally covered by a number of isothermal runs for determining E suffice, *i.e.*, about 20 degrees. Such temperature changes can be obtained in numerous reactions by allowing them to proceed adiabatically to only one-fifth completion. Despite the inaccuracies inherent in the graphical evaluation of the above logarithmic expressions (involving the drawing of tangents to suitable graphs), it may be possible, because of the outstanding accuracy of thermometric measurements, actually to exceed the accuracy with which the mass law constants are determinable from the conventional isothermal straight-line plot in individual cases.

Concerning the listed assumptions individually, the following remarks will suffice. Constant deviations of the activity coefficients from unity (as postulated in assumption (1)) affect our mathematical treatment only in a trivial manner. As regards assumption (2), it is clear that the adiabatic technique provides no separate verification of the Arrhenius law but has to assume its validity. But in cases which are found to be reasonably accurately described by our equations, it is hardly conceivable that we should be misled by mutually cancelling errors into more than minor deviations in the measured reaction parameters. The Arrhenius law has been found almost universally to be so well obeyed through temperature ranges such as we require (in homo- and heterogeneous, catalyzed and uncatalyzed reactions), that more ingenuity has had to be expended on explaining the fact of its accurate verification than departures therefrom.

Assumption (3*b*) is probably the most troublesome, since it excludes from the adiabatic technique—in the simple form here given—such composite and complicated reactions as have provided the masterpieces of elucidation of isothermal kinetics. It must be admitted that if the kinetics are complicated (thus invalidating assumption (3*b*)) the mathematical inconvenience of allowing the temperature parameter to vary far outweighs any experimental advantage the adiabatic technique may provide. But though it may fail to disentangle the elementary steps of complicated reactions, it may yet serve to measure overall activation energies which are occasionally measured isothermally for such reactions as vinyl polymerization. Assumptions (4) and (5) are not thermodynamically independent in the sense that if the reactant and resultant system have the same specific heat, the heat of reaction cannot vary with temperature; both assumptions are, moreover, commonly made in physicochemical work covering temperature ranges as limited as are here required.

Regarding assumption (6), it may be stated that, with proper technique, adiabatic conditions are easier to achieve than isothermal conditions. An isothermal technique requires heat exchange between the reacting system and the surroundings, and this factor leads one to reduce the size of the system. Adiabatic conditions, on the contrary, are favored by increasing the size of the reacting mass, to minimize heat transfer. Such transfer can, moreover, be practically eliminated by jacketing and controlling the jacket temperature electronically to correspond with that of the system.

It is true that the necessity of truly adiabatic conditions entails the need for thermometers of very low heat capacity. These are found among electrical instruments, both thermocouples and resistance thermometers; for accuracy

and low heat-capacity the socalled Thermistor is outstanding. These instruments allow an accuracy to 0.0001°. It follows that, in principle, an adiabatic reaction covering only 10° C should be measurable to within one part in 10^5, which compares very favorably with the accuracy of, say, chemical titration used in isothermal experiments. It is also possible to amplify accurately thermoelectric currents by a combination of photoelectric and electronic principles[2]. The relative freedom from inertia and time-lag of such systems would be valuable in relatively fast reactions; the advantages could be enhanced by replacing the galvanometer by an oscillograph. As already mentioned, the current—once amplified—can be differentiated with respect to time by suitable induction circuits.

Despite the favorable conclusions of this brief discussion, it appears as yet a matter for speculation whether an adiabatic technique can be generally developed (at least in kinetically straightforward reactions) to become a complementary tool to the conventional one. The same reservation is not made in respect of the kinetics polymer chemistry in which the author hopes to justify the employment of his method.

APPLICATIONS TO THE KINETICS OF POLYMERS

The argument for the employment of the adiabatic method in polymer chemistry rests on the following considerations.

(1) The isothermal technique is generally rendered difficult by the intractability of polymers (insolubility or slow rate of solution, high viscosity, etc.) and by the accumulation of the reaction heat. Thus Norrish and Brookman[3], working on the polymerization of styrene and methyl methacrylate, find an unavoidable **S**-shaped temperature rise of 20° C in a thermostatted polymerizing system of only 2 cc. in volume. Neither conduction nor convection is effective in the gelatinous polymer for dissipating the reaction heat; this is stated[4] to limit the determination of E.

(2) As a result of these difficulties thermal studies are already used as an approach to kinetics in this field; though little attempt seems to have been made to elaborate these studies on a mathematical basis or to evaluate the reaction parameters. Bruce, Lyle and Blake[5] in a paper on vulcanization specifically state that the "heat effect during a chemical reaction frequently assists in the understanding of its mechanism". Brickwedde[6] investigated styrene polymerization by its adiabatic heat effect, and thus measured its energy of activation.

(3) Existing data often demonstrate the *a priori* suitability of an adiabatic technique, though insufficient attention has generally been paid to strictly adiabatic conditions for a direct working up of published material. In at least two fields, **S**-shaped heating curves with temperature rises of over 100° C have been observed. One is the field of vinyl polymerization already mentioned[7], the other is that of catalyzed phenol- and cresol-formaldehyde resins[8].

(4) In a subsequent paper an example is worked out to illustrate, on the basis of existing data, the applicability of the technique to the kinetic analysis of the vulcanization of butadiene-styrene copolymer with sulfur. The author is planning further experimental work in the field of the vulcanization of rubbers. In conclusion, he would plead for the publication of relevant measurements, already in existence, on any chemical reactions.

SUMMARY

Conventional kinetic measurements, based on isothermal reaction runs, have hitherto been used to evaluate the reaction parameters required for the description of a chemical rate process. These parameters are the order n of the reaction, its activation energy E, and its frequency factor X. A new technique is here proposed in which adiabatic reaction runs are employed. The temperature change is used to follow the reaction progress. The theory of the heat-effect of adiabatic reactions is deduced, and the mathematical working-up of adiabatic time-temperature data for the evaluation of n, E and X is set out on the basis of stated assumptions. A critical discussion of the method follows, and shows that it is of particular value in polymer chemistry and wherever viscous rubbery or solid reaction media are encountered. The difficulties of heat exchange associated with isothermal measurements are avoided. To what extent the proposed method may be complementary to the conventional in general appears as yet a matter of speculation.

ACKNOWLEDGMENT

The author desires to thank Prof. H. W. Melville for his kind encouragement and helpful criticism.

REFERENCES

[1] Bartlett and Altschul, *J. Am. Chem. Soc.* **67**, 817 (1945).
[2] *J. Scientific Instruments* **22**, 218 (1945).
[3] Norrish and Brookman, *Proc. Roy. Soc.* **A171**, 147.
[4] Norrish and Brookman, *Proc. Roy. Soc.* **A171**, 162.
[5] Bruce, Lyle and Blake, *Ind. Eng. Chem.* **36**, 37 (1944).
[6] Brickwedde, *India Rubber World* **1946**, p. 227.
[7] For a graph unfortunately insufficiently documented (see *Industrie de plastiques* [2] **2**, 42 (1946)).
[8] Unpublished observations by the present author.

ADIABATIC REACTION KINETICS OF BUNA-S VULCANIZATION *

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In a previous paper[1] a technique for making kinetic measurements adiabatically instead of isothermally was discussed, and the possible advantages of this technique in reactions involving polymers was indicated. In the present communication, the theory is supported by an analysis of published data relating to the vulcanization of butadiene-styrene copolymer.

There are considerable gaps in our knowledge of the overall chemical changes concerned in the vulcanization of various rubbers, quite apart from the kinetic interpretation of rate measurements and the postulation of elementary steps. Because of the difficulties involved, isothermal rate measurements have not yet given much insight into the kinetics or the chemistry of the time-honored sulfur vulcanization discovered over a hundred years ago. The difficulty of maintaining the temperature constant against the considerable heat of reaction is only one of the obstacles; that of finding a convenient and accurate measure of the progress of vulcanization considered as a chemical reaction is perhaps even greater. The difficulties of the adiabatic technique are essentially different in nature.

Only conclusions of a preliminary kind are reached in this paper, largely because existing data are meager. Nonetheless, the fact that under suitable conditions first-order kinetics are obtainable is quite firmly established. This must be contrasted with the early measurements by Spence and Young, quoted by Williams[2], which indicated that the isothermal vulcanization of natural rubber is a zero-order reaction, the rate of which depends on the initial amount of sulfur. The activation energy of Buna-S vulcanization is here found to be approximately 32,000 calories, which is in agreement with previous estimates. A frequency factor of 1.9×10^{14} min.$^{-1}$ is calculated. The meaning of these kinetic parameters, accepted provisionally as correct, is discussed below, and agreement with the views of Meyer and others on the mechanism of vulcanization is reached.

The time–temperature data to be considered are those graphed by Bruce, Lyle, and Blake[3], and refer to their experiment with Buna-S compounded with 6 per cent sulfur. Of all the heating curves obtained during the vulcanization of rubbers[4], this particular one seems to approximate most closely true adiabacity, and measurements were specifically undertaken because the "heat effect during a chemical reaction frequently assists in the understanding of its mechanism".

The size of the Buna-S sample employed was sufficient to warrant Blake's conclusion[5] that the overall temperature rise obtained would not have been very much larger if the size had been further increased; also the bath temperature employed was about midway between the initial and final temperatures of

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the adiabatic reaction. Nonetheless, instead of approaching a final maximum temperature, the graph consists of a heating branch, rising to a peak, followed by a shallow cooling branch. It is apparent that this deviation from adiabacity may—as a good approximation—be neglected if one compares the slopes of the two branches at equal temperatures. For highly accurate data a correction could be applied on the basis of such a comparison. The experimental points from the graph in question are shown in Figure 1, which has been obtained by accurate photographic reproduction and enlargement. The smooth graph drawn by the original authors has been deleted and the theoretical equation:

$$dT/dt = 1.9 \cdot 10^{14}(493 - T)e^{-32,000/RT} \text{ ° K min.}^{-1} \qquad (1)$$

substituted without noticeable change in the accuracy of the fit. The implications of this equation (in which T denotes temperature, and t, the time) are four-fold: (1) the final temperature reached under adiabatic conditions would be 492° K (this figure, important only for the thermochemical implications of the experiment, does not enter further into our kinetic discussion); (2) the activation energy E equals 32,000 calories per mole; (3) the frequency factor X equals $1.9 \cdot 10^{14}$ min.$^{-1}$; (4) the order n of the reaction is unity.

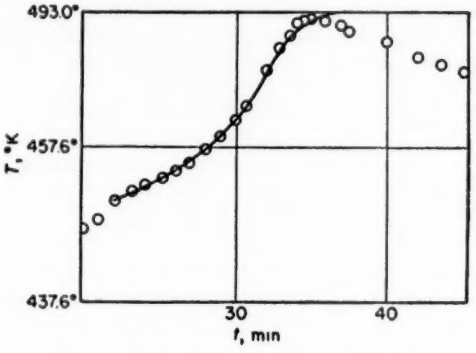

FIG. 1.—Temperature vs. time of vulcanization.

While reference must be made to the earlier paper[1] for the theory underlying the derivation of this equation, the evaluation of the parameters from the experimental data and the integration of the equation will now be discussed in some detail:

Let T_f denote the final temperature, and T^* the temperature of the inflection point ($d^2T/dt^2 = 0$). The two points at which $d^3T/dt^3 = 0$ are T' (below the inflection point) and T'' (above the inflection point). θ will denote $(T_f - T)$ and $V = E/RT$. The following estimates were written down by inspection of the graph of Blake and his coworkers:

$$\begin{aligned} T_f &= 493° \text{ K} & (\theta_f &= 0) \\ T'' &= 489° \text{ K} & (\theta'' &= 4) \\ T^* &= 476.8° \text{ K} & (\theta^* &= 16.2) \\ T' &= 461° \text{ K} & (\theta' &= 32) \end{aligned}$$

These values were substituted in the following theoretical equations[1]:

$$\theta^* = nRT^{*2}/E \qquad (2)$$

$$\theta' = G'nRT'^2/E \tag{3}$$

$$\theta'' = G''nRT''^2/E \tag{4}$$

G' and G'' are given by:

$$G' = \left[1 + \left(\frac{V' + 2n - 1}{2nV'}\right)^{\frac{1}{2}}\right] V'/(V' - 1) \tag{5}$$

$$G'' = \left[1 - \left(\frac{V'' + 2n - 1}{2nV''}\right)^{\frac{1}{2}}\right] V''/(V'' - 1) \tag{6}$$

These functions are tabulated in terms of V and n once and for all; they are largely dependent on the value of n and but slightly on V. Equation (2) was used first to evaluate the activation energy from the estimated inflection point T^*; thus $E = 28{,}100n$ approximately. Now, Meyer states[6] that for natural rubber vulcanization E is about 30,000, and similar values can be calculated from the approximately known temperature coefficient of isothermal Buna-S vulcanization. Therefore, from the inflection point alone we find that if an approximately integral order is to be obtained, this must be a first-order reaction. E was accordingly taken as 28,100 for a first approximation and, using Equations (3) and (4), θ' was calculated to be 26° and $\theta'' = 4.9°$. While these values were only in rough agreement with the estimates listed, the more accurate procedure of a plot based on the first-order law:

$$\ln [-d(\ln \theta)/dt] = \ln X - E/RT \tag{7}$$

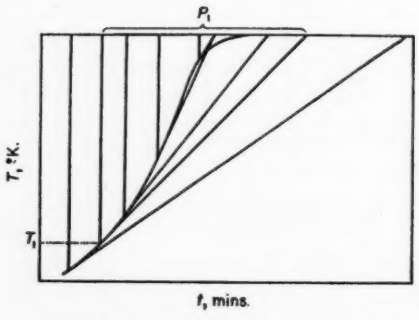

FIG. 2.—Determination of intercepts P (scale same as in Figure 1).

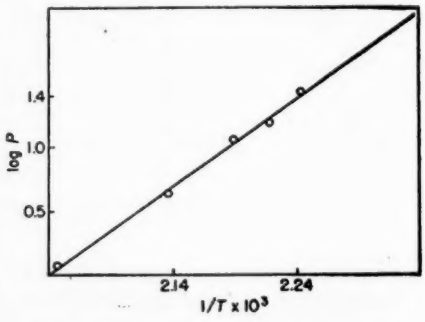

FIG. 3.—Straight-line test for first-order law.

seemed justified. As shown in Figure 2, tangents were drawn to the heating curve at various temperatures, and perpendiculars (lines of constant time) were drawn through each point of tangency. Each tangent and its corresponding perpendicular between them cut off some intercept P on the line $T = T_f$, which is the line asymptotically approached at the end of the experiment. It is easily seen that:

$$1/P = |d(\ln \theta)/dt| \tag{8}$$

Figure 3 shows the plot of log P against $1/T$—an excellent straight line of slope $E/2.3R = 6970$; from the intercept of the plot on the log P axis, frequency factor X was found of the order of 10^{14} min.$^{-1}$. A direct integration

of equation (1) using $E = 32{,}000$ was clearly justified. In integrated form this yields:

$$Xt = Ei(V) - Ei(V_0) + e^{V_f}[Ei(Q_0) - Ei(Q)] \tag{9}$$

where the following abbreviations are used: subscripts refer to the time—zero to the beginning, f to the final time; Q equals $(V - V_f)$, and:

$$Ei(V) = \int_{-\infty}^{V} e^x dx/x \tag{10}$$

For our data V is of the order of thirty, while the integral (Equation 10) appears to have been tabulated only in the range $0 < V < 20$. An expansion in series of (9) was, therefore, used which converges rapidly when $(V - V_0)$ is small compared to V. Writing W for $(V - V_0)$ the series, expanded as far as the first three terms and rearranged, reads:

$$Xt = e^{V_0}/V_0[e^W\{1 + 1/V_0 + 2/V_0^2 - W(1/V_0 + 2V_0^2 + W/V_0^2)\} - (1 + 1/V_0 + 2/V_0^2)] + e^{V_f}[Ei(Q_0) - Ei(Q)] \tag{11}$$

The expression on the right was calculated (using normal procedures of tabulation) at intervals of 4° between $T_0 = 445.8°$ to 489.8° and also at 491.8° ($T_f = 493°$). The resulting curve was superimposed on the experimental points of Blake and his coworkers and is shown in Figure 1; the frequency factor, $X = 1.9 \cdot 10^{14}$ min.$^{-1}$, which enters as a multiplier of the time only, is found—not by calculation—but by adjusting the time scale when superimposing the graph on the experimental data.

In the sequel the values $E = 32{,}000$, $X = 1.9 \cdot 10^{14}$, and $n = 1$ are accepted provisionally as correct for the reaction between Buna-S and 6 per cent sulfur; it is pointed out, however, that the determination of E and X from the graph under discussion is not very high. As in isothermal kinetics, the interdependence of E and X is such that if a higher value of E is chosen, X must also be increased to fit the data. It is estimated that $E = 32{,}000$ may be too low a value by 5 per cent or too high by 10 per cent; correspondingly, $X = 1.9 \cdot 10^{14}$ may be in error by about one or two powers of 10. More accurate adiabatic measurements than those under discussion should, in principle, yield an accuracy in the parameters comparable with that obtainable from a series of isothermal measurements. A high reliance can be placed on the present evaluation of the third parameter, the order n of the reaction. It is clear that no good fit of the experimental points can be obtained with integral values other than unity, and even the best such fit does not yield reasonable values of E or X. The usual caution, however, should be applied in arguing from first-order kinetics to true unimolecularity of reaction. It can now be shown that a reasonable picture of Buna-S vulcanization can be constructed on these kinetic parameters and our general, although somewhat scant, chemical knowledge relevant to the problem. Thus we may assume that, under Blake's conditions, all of the sulfur is in solution in the polymer and that its rate and heat of dissolution plays no part in the thermal changes measured. The reaction leads to the formation of a soft rubber and, as with natural rubber, the heat of reaction is proportional to the amount of sulfur originally present—within wide limits. The unsaturation of the rubber falls linearly with the proportion of sulfur chemically combined. The sulfur is originally present as free S_8 (and possibly S_6) rings, and is finally converted predominantly to thioether and polysulfide sulfur linking carbon to carbon: C—S_x—C.

It is clear from the last fact alone that the vulcanization reaction is complex and cannot merely consist of a single elementary step which is repeated until all the sulfur is exhausted. The first-order kinetics, on the contrary, must be the result of a slow, rate-determining step (one participant of which becomes progressively exhausted until its concentration dies away), which is preceded or followed (or both) by a series of fast steps which complete the overall reaction. Moreover, since we have followed the reaction by the adiabatic heat rise, the heat evolved by all the steps together must be strictly proportional to the progress of the slow step if our measurements are to be significant kinetically. The species whose disappearance is reflected in the slow first-order step can hardly be the polymer or any derivative thereof. This is vouchsafed by the absence of any appreciable steric factor; thus a frequency factor of 10^7 rather than 10^{14} might reasonably be expected in a reaction involving a polymer. Moreover, the reactive positions in the polymer are far from exhausted by the 6 per cent sulfur employed; whence a locally activated polymer is excluded as the disappearing species. The sulfur, on the other hand, is substantially combined at the end of the reaction, and the reactive species must be some form of sulfur. Early theories of natural rubber vulcanization have often centered on the interconversion of various forms of sulfur, and atomic sulfur has been invoked as a reactive intermediate. Consideration of energetic factors shows conclusively that the slow step with an activation energy of 32,000 must lie near the beginning of the sulfur breakdown, since the breaking of an S_8 ring into 8 atoms requires some 400,000 calories per mole. The amount of S or even S_2 in equilibrium with S_8 rings must be infinitesimal, and, accordingly, their concentrations, even if produced by fast steps, would vary either as the eighth or fourth root of the sulfur concentration, respectively, under isothermal conditions (or as a first approximation under adiabatic conditions). First-order kinetics are thus not possible if the activated species is imagined to be a sulfur atom. This is stressed because the absence of a steric factor (or entropy term) implied in the value of X here deduced might seem to render the atomic hypothesis attractive and support for it might be sought in the fortuitous fact that atomic sulfur has an activated state 36,000 calories above the ground level.

A clear hint comes to our aid from the classic work of Meyer on the polymerization of sulfur which is the basis of the rubbery or plastic state of the element. He writes[7]: "It is to be noted that in the absence of accelerators, vulcanization begins to take place at the same temperature at which pure molten sulfur begins to transform into amorphous sulfur. In the process active nuclei, consisting perhaps of S_8 chains with free valences, are formed and will certainly react rapidly with olefins." The idea is taken further by Farmer[8], who discusses in detail the (relatively short) series of fast steps that follow on each such thermal scission of a sulfur ring.

If the unimolecular reaction:

$$S_8 \text{ (ring)} \longrightarrow S_8 \text{ (chain biradical)}$$

is to be the rate-determining step in the vulcanization of Buna-S under Blake's conditions, it remains to account for the deduced frequency factor and activation energy. The value found for the former is—as it ought to be—or the order of magnitude of a molecular vibration frequency. It is not considered that any marked entropy factor would be expected to slow down the proposed scission, since all the atoms and bonds in the S_8 ring are equivalent. Provided any one of the eight sulfur atoms is sufficiently energized by collision, its two

bonds would be strained before the energy could become distributed around the ring.

The activation energy of a short-chain reaction initiated by a unimolecular primary act should be approximately equal to that of the primary act itself. The activation energy of the suggested primary act, *i.e.*, the splitting of an S_8 ring, should be only very slightly greater than its heat of reaction. The two statements may be summed up by saying that the activation energy of vulcanization should, on the proposed mechanism, be very slightly above the heat of reaction of the splitting of an S_8 ring. Powell and Eyring have estimated this heat of reaction[9] to be 27,500 ± 5000 calories. Thus the activation energy of 32,000 calories here deduced for the vulcanization reaction under discussion, as well as the frequency factor and the order of the reaction, is in quantitative agreement with the hypothesis that the rate-determining step is the splitting of an S_8 ring.

The application of the adiabatic technique to vulcanization is favored by the circumstances that the simple primary act is followed by a chain of reactions, which—however complex—liberate on the average a constant amount of heat. This conclusion is supported by the known facts that the unsaturation and the heat of vulcanization change linearly with the proportion of sulfur employed. The simplicity of the primary act, moreover, appears to resolve the paradox that so complex a radical reaction as vulcanization could be so early got under control by the empiricism of rubber enthusiasts. The writer is engaged in experimental work to extend the application of adiabatic kinetics in the polymer field, *e.g.*, to accelerated vulcanization.

SYNOPSIS

The adiabatic technique of making kinetic measurements has been applied to published time–temperature data concerning the vulcanization of Buna-S with 6 per cent sulfur. The kinetic parameters of the rate-determining step are calculated within stated limits of accuracy; the rate-determining step is thereby identified as the reaction S_8 (ring) → S_8 (chain biradical) which has been speculatively advanced as the first step in vulcanization by some investigators.

ACKNOWLEDGMENT

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REFERENCES

[1] Gordon, *Trans. Faraday Soc.*, in press.
[2] Williams, *Ind. Eng. Chem.* **39**, 902 (1947).
[3] Bruce, Lyle, and Blake, *Ind. Eng. Chem.* **36**, 37 (1944).
[4] For earlier curves on natural rubber, see Perks, *J. Soc. Chem. Ind.* **45**, 142T (1926).
[5] Blake, *Ind. Eng. Chem.* **26**, 1283 (1934).
[6] Meyer, "Natural and Synthetic High Polymers", New York, **1942**, p. 139.
[7] Meyer, "Natural and Synthetic High Polymers", New York, **1942**, p. 140.
[8] Farmer, *J. Soc. Chem. Ind.* **66**, 87 (1947).
[9] Powell and Eyring, *J. Am. Chem. Soc.* **65**, 648 (1943).

PROGRESS IN POLYMERIZATION THEORY OF INTEREST IN SYNTHETIC RUBBER PRODUCTION *

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Introduction.—During the last few years considerable advances have been made in the theory of polymerization processes, and these have a direct bearing on the manufacture of synthetic rubbers and plastics and the properties of the various products of this type that are now handled by the rubber industry. The most important industrial process involves emulsion polymerization. This is used in the production of types, such as GR-S, Perbunan, and Neoprene, and also in the production of polyvinyl chloride. World production of these emulsion polymeric materials is in the region of hundreds of thousands of tons per annum, and the process is probably one of the more important chemical manufactures developed in the last decade. No large manufacture of synthetic rubber has been developed in Great Britain, mainly because of war-time exigencies and economic considerations, and the only significant contribution made by British chemical industry to alleviate the war-time scarcity of natural rubber was to develop a large-scale production of polyvinyl chloride to satisfy the requirements of the cable trade[1].

There has, however, been some research activity on synthetic rubber in this country since 1935 in the laboratories of the Dyestuffs Division of Imperial Chemical Industries, Ltd. Activity in the main was concentrated on the diene emulsion interpolymer types and a large number of second components were examined for interpolymerization with both butadiene and chloroprene. Comparatively few interpolymerize to give rubbers with reasonably good vulcanizate properties. These have been disclosed in the patent literature[2].

Parallel work was being carried out in the laboratories of I. G. Farbenindustrie and later in America, and the results of much of this have now appeared in the technical literature and in the accounts that are now available on German war-time activities. The general conclusions were similar.

Early laboratory assessment indicated that a promising candidate as an abrasion-resisting rubber is the interpolymer of butadiene with methyl methacrylate[3], and it is interesting to note now that the I. G. were developing this type in Germany towards the end of the war as Buna-M. Among the best oil-resistant types is the interpolymer of chloroprene with cyanoprene[4] and a small-scale manufacture of this was undertaken in this country in improvised plant during the early stages of the war because a highly oil-resistant rubber was essential in aircraft production. This was handled by the rubber trade in this country as Neoprene-Z. The only other suitable product was the Buna-N made by I.G., which, of course, was not available to us at that time. Effort was not confined to the diene rubber types; other high polymers with rubber-

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 23, No. 5, pages 219–230, February 1948.

like properties were also explored, and this gave rise to the ester rubber which is now being marketed as Vulcaprene.

During the course of these investigations much information was collected on the polymerization features which affect both the polymerization speed and the properties of the rubbers, and the object of this paper is to survey this aspect of the work.

For example, in a butadiene interpolymerization process, there is a large number of individual reaction steps occurring simultaneously, and their relative speeds govern not only the rate of polymer production but also have a direct effect on the molecular structure of the resulting polymer and, therefore, on those properties which are of technical interest.

The polymerization recipes used include, in addition to the two monomers, an aqueous solution of an emulsifying agent, usually an organic sulfonate or a soap; a peroxy catalyst, such as hydrogen peroxide, perborates or persulfates or in some cases oxygen itself; a chain transfer agent, such as dodecanethiol, carbon tetrachloride, or diisopropylxanthogen disulfide; sometimes a buffer, such as sodium borate or phosphate; and, in the more modern recipes, there may be present a reducing agent such as sulfite or glucose; finally additions may be made of a small percentage of a metal salt or complex, usually iron or copper.

The reactions occurring during the polymerization are complex and there are many individual reaction steps, most of them simultaneous. There are at least two reactions which involve the catalyst system and give rise to the free radicals which initiate polymerization. These are followed by the initiation reactions which involve reaction of the free radicals with either monomer. Then there are the propagation reactions, of which there are four main types. As the butadiene can add on by either a 1,4-addition or a 1,2-addition, there are in all nine possible reaction steps. There may be further types of addition if we consider the possibilities of head-to-head and head-to-tail configurations. The chain transfer agent also interacts with all these propagating steps, giving another series of reactions and, finally, there is the series of terminating reactions, at least three in number, but probably many more.

In addition, it must be remembered that all these reactions take place in a heterogeneous system and they may occur either in the water phase or the monomer phase or at the aqueous, nonaqueous interface. Therefore. there can be up to a 100 simultaneous reaction steps, and this leaves out fine differences in the propagation reactions as the chains grow longer. The object of research in synthetic-rubber production is to balance and control these reactions so as to attain the most favorable polymer molecular structure for optimum technically valuable properties.

In a simple vinyl polymerization, such as the polymerization of acrylonitrile dissolved in water, initiated by collision of a free radical with a monomer molecule and terminated by interaction of two growing chains, the rate of polymerization when stationary state conditions are attained is given by:

$$-\frac{dm}{dt} = k_p \sqrt{\frac{k_i r}{k_t}}\, m^{1.5}$$

and the chain length of the polymer being formed at any given time is:

$$\nu = 2k_p \sqrt{\frac{m}{k_i k_t r}}$$

where m is the monomer concentration, r the free radical concentration, and k_i, k_p and k_t are the velocity constants of the initiation, propagation and termination reactions.

We can now use this simple polymerization system as a basis for analyzing what is happening in the more complex emulsion interpolymerization.

Initiation reactions.—The initial opening of the monomer double bond is usually effected in a vinyl type free radical polymerization by the use of peroxy compounds, such as benzoyl peroxide, hydrogen peroxide or persulfates. It is almost certain that they act by giving rise to free radicals. For example, benzoyl peroxide decomposes by the following reaction:

$$(C_6H_5CO_2)_2 \rightarrow CO_2 + C_6H_5- + C_6H_5CO_2-$$

and the free radicals formed react with the monomer in the following manner.

$$R- + CH_2 = CHX \rightarrow R-CH_2 - CHX-$$

The important catalysts for the emulsion processes used for the butadiene interpolymer rubbers, Neoprene and polyvinyl chloride are the water-soluble persalts and peroxides such as ammonium or potassium persulfate, perborates, and hydrogen peroxide. The persulfates are the most commonly used. Persulfates do not decompose in aqueous solution at a fast enough rate to account for the initiation of the polymerization by free radicals arising from a spontaneous decomposition[6], and no adequate mechanism has yet been published that gives a quantitative picture. More is known of the most recent method of initiation of polymerization. This has been termed in this country "reduction activated" polymerization and in Germany "Redox" polymerization.

The effect is produced by adding to a peroxy-catalyzed polymerization a suitable reducing agent[7]. This induces a considerable increase in the polymerization rate. For example, with vinyl chloride, polymerization can be effected in a few minutes[8], whereas previously it had taken many hours.

The mechanism of the effect has been studied, using the acrylonitrile system as the reference polymerization and using as the catalyst pair persulfate and thiosulfate[6] and ferrous ion and hydrogen peroxide[9].

In both cases two molecules of the reducing agent react with one molecule of the oxidizing agent, and there are two consecutive reactions involving the intermediate formation of a free radical:

$$Fe^{++} + H_2O_2 \xrightarrow{k_1} Fe^{+++} + OH^- + OH$$

$$Fe^{++} + OH \xrightarrow{k_2} Fe^{+++} + OH^-$$

A similar mechanism occurs in the persulfate, thiosulfate reaction giving rise to a free radical which might be either $-SO^-_4$ or OH.

The stationary state concentration of the free radical in the presence of polymerizing monomer is then given by:

$$r = \frac{k_1[\text{oxidizing agent}][\text{reducing agent}]}{k_2[\text{reducing agent}] + k_t m}$$

It will be seen that the value of r and, therefore, the rate of the induced polymerization is increased if k_1 is increased. Addition of a catalyst for the reaction between the oxidizing agent and the reducing agent is in effect equivalent to doing this. Powerful catalysts for the reaction of persulfate with thiosulfate are to be found among metallic ions with a changeable valency.

Thus addition of a few parts per million of Cu^{++} has a considerable effect on this reaction rate, and the resulting increase in r is reflected by an enhanced polymerization rate[10]. In other words Cu^{++} is a promotor of polymerizations catalyzed by the persulfate, thiosulfate reduction activation pair.

Promoters of this type, although they increase the concentation of R and therefore effect a more rapid polymerization, also reduce the lifetime of the reacting system. Thus the addition of too much promoter results in very rapid initial polymerization followed by a complete cessation of polymerization, and it is necessary to adjust the recipe so that the reaction between the peroxy compound and the reducing agent does not go to completion before polymerization is complete.

Using water-soluble pairs such as persulfate-thiosulfate or persulfate-sulfite, the activity for initiation of polymerization in emulsion has varied considerably with the monomer. They are particularly active with vinyl chloride[8], methyl methacrylate[11], and acrylonitrile[11], but have little effect on butadiene and styrene. Thus it has been found that this type of reduction activated recipe is not markedly effective in promoting the interpolymerization of butadiene and styrene, but is so for interpolymerizations of butadiene with either acrylonitrile or methyl methacrylate[12]. In the latter cases the initiation reaction and therefore, the overall polymerization rate is enhanced by the reduction activation effect on the acrylonitrile and the methyl methacrylate.

There is some evidence for believing that the seat of the butadiene emulsion interpolymerization is at the aqueous, nonaqueous interface and, therefore, an attempt was made to locate as far as possible the interaction of the persulfate and the reducing agent to the interface. This was achieved by using as the reducing substance an organic tetravalent sulfur compound that might be expected to be more soluble in the nonaqueous phase than the inorganic salts previously used. The most active compounds found were dialkyl sulfoxides. The addition of these to butadiene and styrene interpolymerization caused marked acceleration[13]. Polymerization rates were achieved by this means which were comparable with those attained independently in Germany by using their Redox formulations.

Preferred Redox formulations for butadiene interpolymerizations consist of the use of a reducing agent and an oxidizing agent, one of which is oil-soluble and the other water-soluble[14]. It is immaterial which agent is water- or oil-soluble. Examples of pairs used were persulfates and aromatic aldehydes; and perbenzoic acid and dihydroxyacetone or glucose. It was also preferable to have present a small amount of metal with a changeable valence. These are just the conditions which the above theory on reduction activation had indicated to be most favorable for obtaining the optimum effect.

The advantage of reduction-activation over the conventional polymerization method is that it not only speeds up the polymerization process but also permits the process to be carried out in a reasonable time at much lower temperatures.

Lowering the polymerization temperature tends to give a more linear less branched polymer structure because the undesirable reactions which lead to branching can be expected to have a higher temperature coefficient than the normal propagation reactions which give the linear unbranched structure.

The propagation reactions.—During the last few years there has been considerable attention paid to the kinetics of the interpolymerization of two monomers in homogeneous systems, and this is now one of the more active fields of research within the polymer field.

The manner in which the interpolymerization proceeds is of particular importance where polymerization control is required to achieve the best physical properties. It is obvious that a preferential polymerization of one component results in an interpolymer heterogeneous in character and with poor physical properties. In, say, the interpolymerization of butadiene with a second component such as styrene or methyl methacrylate, this is easily seen to be so. Polystyrene or polymethyl methacrylate are far from being rubberlike in properties, and polybutadiene made in an emulsion system is a very poor rubber indeed. Therefore the aim of interpolymerization of these components is to achieve as uniform an interpolymer as possible so as to be as far removed as is feasible from the undesirable extreme. The rates at which monomers disappear relative to one another in an interpolymerization system vary considerably from pair to pair. The relative rates of disappearance in the case of the pairs butadiene–styrene, butadiene–methyl methacrylate, butadiene–acrylonitrile and chloroprene–cyanoprene are not so great as to cause marked heterogeneity in the resulting interpolymer, although there are small differences between them which result in effects on the rubberlike properties due to differences in the distribution of the monomer units in the interpolymers. In other cases, *e.g.*, chloroprene–acrylonitrile, one monomer polymerizes much faster than the other, and to obtain the best effect both in rubberlike properties and in the utilization of the slower polymerizing monomer it is desirable to add the faster polymerizing monomer stepwise during the interpolymerization.

In an interpolymerization involving monomers A and B, there are four main types of propagation steps. These are:

$$\underset{(\alpha)}{\sim A\!-} + \underset{(a)}{A} \xrightarrow{k_p{}^a} \sim A\!-$$

$$\underset{(\beta)}{\sim B\!-} + \underset{(b)}{B} \xrightarrow{k_p{}^b} \sim B\!-$$

$$\sim A\!- + B \xrightarrow{k'} \sim B\!-$$

$$\sim B\!- + A \xrightarrow{k''} \sim A\!-$$

When stationary state conditions are attained, the ratio of monomers entering the polymer, or the composition of the polymer being formed at any given instant, is given by:

$$\frac{da}{db} = \frac{a}{b} \cdot \frac{k^{11}}{k^1} \frac{k_p{}^a a + k^1 b}{k_p{}^b b + k^{11} a}$$

This equation for interpolymer composition has been derived and tested in nonemulsion interpolymerizations by American workers[15].

The last two reactions are the ones we wish to favor if we require homogeneous interpolymerization. In the work carried out in the laboratories of the Imperial Chemical Industries, Ltd., the assumption was made that the interpolymerization propagation constants were equal, *i.e.*, $k^1 = k^{11} = k_p{}^c$. This simplification makes it easier to appreciate the general effect of the interpolymerization tendency on the course of the overall polymerization and the

homogeneity of the resulting polymer, and is justifiable here as we merely wish to have a qualitative picture of the interpolymerization tendencies in the more complicated emulsion interpolymerization system. The simplified formula is:

$$\frac{da}{db} = \frac{a}{b} \cdot \frac{k_p{}^a a + k_p{}^c b}{k_p{}^b b + k_p{}^c a}$$

As the interpolymerization proceeds and monomers are used up at different rates, there is a drift in the value of a/b, which results in a variation in the composition of the interpolymer formed with time.

In some cases there is one value of a/b, depending on the relative values of the constants involved at which the constitution of the polymer being formed is the same as the constitution of the monomer mixture.

These conditions are attained if $\frac{k_p{}^a a + k_p{}^c b}{k_p{}^b b + k_p{}^c a}$ is unity, *i.e.*, when $\frac{a}{b} = \frac{k_p{}^c - k_p{}^b}{k_p{}^c - k_p{}^a}$. A polymer formed under such conditions has been termed by Wall an "azeotropic copolymer"[16].

This "azeotropic" interpolymerization condition cannot be attained if either $k_p{}^b$ or $k_p{}^a$ are $> k_p{}^c$ because the value of a/b is a negative imaginary value. A simple case is when $k_p{}^b$ and $k_p{}^a$ are zero. This holds for the emulsion interpolymerization of isobutylene and diethylfumarate, and azeotropic interpolymerization conditions are attained when the monomers are present in molar ratio. If there is a higher ratio of isobutylene to diethyl fumarate than unity, then the polymer formed from molecular equivalents leaves a residual monomer ratio with an increasing amount of isobutylene, and *vice versa*.

In the butadiene emulsion interpolymerizations studied in detail in the laboratories of Imperial Chemical Industries, Ltd., using uncatalyzed emulsion recipes only the system butadiene–methyl methacrylate behaved as if it had a value of $k_p{}^c$ larger than $k_p{}^a$ or $k_p{}^b$ and azeotropic interpolymerization conditions were attained with about 60 per cent by weight of methyl methacrylate in the monomer mixture. When the methyl methacrylate content of the initial monomer mixture was less than this, the polymer formed had a higher methyl methacrylate content than the initial monomer mixture.

The butadiene interpolymerizations with dimethyl fumarate and with acrylonitrile behaved as though $k_p{}^b$ (B = butadiene) was of the same order as, or even larger than, $k_p{}^c$, and $k_p{}^a$ was smaller than $k_p{}^c$, it being observed that the polymer formed contained less of the second component (A) than in the initial monomer mixture. This was observed for interpolymerizations in which the initial monomer mixture contained between 15 to 80 per cent of acrylonitrile. That is, azeotropic interpolymerization conditions either could not be attained with this system because $k_p{}^c$ was smaller than $k_p{}^b$, or $k_p{}^c$ was only slightly greater than $k_p{}^b$ and would only give azeotropic polymerization conditions when less than 15 per cent of acrylonitrile was present in the monomer mixture. It has recently been reported that azeotropic interpolymerization has been obtained with an emulsion interpolymerization of butadiene and acrylonitrile at a molar ratio of 1.6 butadiene to 1 acrylonitrile, *i.e.*, with 32 per cent of acrylonitrile in the initial monomer mixture[17]. This discrepancy is probably due to differences in the polymerization recipes employed. Catalyzing the interpolymerization with a water-soluble persulfate would tend to increase the aqueous phase polymerization of acrylonitrile which would be reflected by an increase in $k_p{}^a$. It is thus possible that a pseudo-azeotropic polymerization is set up in this case, where both $k_p{}^a$ and $k_p{}^b$ are larger than $k_p{}^c$.

The rate of interpolymer formation, as might be expected, varies with the ratio of polymerizing monomers. Assuming a mutual chain terminating process, and assuming that the three possible terminating processes:

$$\left.\begin{array}{l} \sim A- + \sim A- \longrightarrow \\ \sim B- + \sim B- \longrightarrow \\ \sim A- + \sim B- \longrightarrow \end{array}\right\} \text{dead polymer}$$

have the same rate constant k_t, the rate of polymer formation is given by:

$$-\frac{dm}{dt} = \sqrt{\frac{(k_i^a a + k_i^b b)r}{k_t}} \times \frac{k_p^a a^2 + 2k_p^c ab + k_p^b b^2}{m}$$

If in addition k_i^a and k_i^b, which are the rate constants for the initiation of chains by reaction of free radical R with monomers A and B, respectively, are not very dissimilar, then the effect of monomer ratio on the rate of polymer formation is entirely dependent on the relative values of k_p^a, k_p^b and k_p^c. If k_p^c is much larger than k_p^a or k_p^b as in the case of isobutylene–dimethyl fumarate emulsion interpolymerization, or somewhat larger, as in the case of butadiene–methyl methacrylate uncatalyzed emulsion interpolymerization, the rate of polymerization has a maximum value at an initial monomer ratio corresponding to that for azeotropic interpolymerization conditions.

If k_p^b is of the same order as, or greater than k_p^c, and k_p^a is small, as is the case for uncatalyzed emulsion interpolymerization of butadiene with dimethyl fumarate and with acrylonitrile, the rate of polymer formation falls with decreasing butadiene content of the initial monomer mixture. Qualitatively, this is what has been observed for these uncatalyzed emulsion interpolymerizations.

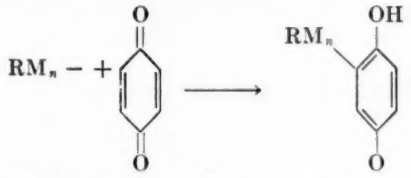
If k_i^a and k_i^b are unequal, the maximum rate does not occur at the monomer ratio corresponding to azeotropic interpolymerization. Thus, addition of water-soluble catalysts and particularly water-soluble reduction activation pairs increase k_i^a in the case of butadiene–acrylonitrile emulsion interpolymerizations. In addition, they increase the amount of aqueous phase polymerization of the second component, and this can be qualitatively expressed in the above formulation as an increase in k_p^a. This results not only in a change in the rate of polymerization monomer ratio curve, but, as pointed out previously, also can give pseudoazeotropic interpolymerization conditions, where the monomer ratio in the residual monomer mixture remains constant during polymerization but the polymer formed is heterogeneous. Strong reduction activation of butadiene interpolymerizations with persulfate and bisulfite, particularly at temperatures above 35° C, gives products consisting of resinous particles dispersed in a rubber matrix.

It is, therefore, readily appreciated that relative rates of consumption of the two monomers are not the criteria for degree of homogeneity of the resulting interpolymer. The governing factor is the relative value of k_p^c to k_p^a and k_p^b, and this is inherent in the monomer pair and the type of polymerization environment. Thus, if the propagation constants have not the appropriate relative values, as is the case say, with, butadiene and vinyl chloride in emulsion, no major improvement can be achieved by changing emulsion polymerization factors. The degree of homogeneity in emulsion systems which do have reasonable relative values of the propagation constants can be affected by either stepwise addition of the faster polymerizing monomer, by stopping the polymerization at an early stage, and also by selecting conditions which reduce any

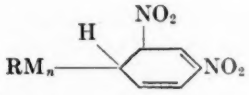
tendency for the monomers to polymerize in different phases. It is possible that the relative values may be altered by changing the polymerization temperature, but it is difficult to establish whether this is so because of the important effect temperature has on other masking reactions such as chain branching.

A major effect can be achieved by changing the environment or the type of polymerization. For example, with butadiene and methyl methacrylate, k_p^c is $>k_p^a$ and k_p^b in uncatalyzed emulsion systems, but k_p^a is $>k_p^c$, and k_p^b is very small in benzoyl peroxide-catalyzed mass or solution interpolymerizations. The trend in synthetic-rubber research, however, has been to search for a diene and second component pair that have favorable values of the propagation constants in an emulsion environment rather than to devise new polymerization techniques that alter either the environment or the structure of the propagating chain end and, therefore, the propagation constants. The reason for this is undoubtedly the lack of success that has attended attempts to induce interpolymerization in pairs that fail to interpolymerize in emulsion by changing to other known polymerization techniques such as sodium or Friedel and Craft catalyzed polymerizations. One exception, however, is the interpolymer of butadiene and isobutylene or Butyl rubber. In the emulsion interpolymerization of butadiene with isobutylene, k_p^b is normal but k_p^c is insignificant and k_p^a is zero, and the resulting polymer is practically normal butadiene emulsion polymer. Changing the polymerization to low-temperature Friedel and Craft catalyzed polymerization changes the relative values of the propagation constants and $k_p^a > k_p^c \geqslant k_p^b$, and it is possible to make an interpolymer containing butadiene and isobutylene, the product containing less butadiene than was present in the initial monomer mixture.

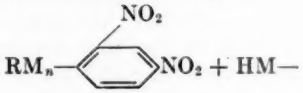
The termination reactions.—In addition to the mutual chain termination reactions mentioned previously, in which the two free radical chain ends combine, termination can occur due to collision with a variety of substances present in the system either as deliberate recipe additions or as fortuitous impurities. A current view is that they add on the free radical chain end, giving a more or less stable free radical configuration. Thus with the polymerization inhibitor benzoquinone, the chain ending mechanism is:



With a weaker inhibitor, such as *m*-dinitrobenzene, a less stable configuration is formed:



This slowly reacts with further monomer to give:



and a new chain is initiated[18].

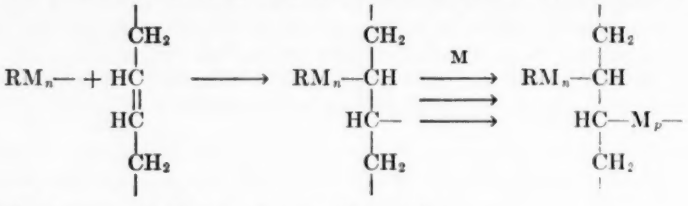
Other chemical species can terminate a polymer chain and either react quickly with further monomer in this way or even give off a new free radical, which can initiate another chain. Thus when carbon tetrachloride is present in the system, the following reactions occur:

$$RM_n— + CCl_4 \longrightarrow RM_nCCl_3 + Cl—$$
$$Cl— + M \longrightarrow ClM—$$

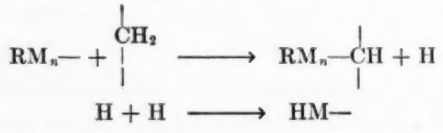
This is not chain termination. It is true a growing polymer chain is rendered inactive, but the growing chain end is transferred to a new polymerizing molecule and the kinetic chain length, or the number of monomer molecules polymerized for each original act of initiation, may be little affected. It is convenient to treat these chain transfer reactions with the termination reactions because it now appears that chain transfer agents and chain terminating agents differ only in the relative stability of the free radical addition products they tend to form with the growing chain end.

The chain terminating effect is to reduce both the molecular weight of the polymer and the rate of polymer formation, while the chain transfer effect reduces the molecular weight, without any marked reduction in the rate of formation of polymer. Chain-transfer agents are of considerable importance in the manufacture of diene synthetic rubbers because, in the first place, they enable the molecular weight to be controlled without increasing the time of polymerization. Too high a molecular weight gives a tough product which has to be broken down to a workable plastic material before compounding. There is, however, a more important effect of these chain transfer agents on the polymer structure which will become clear when we consider the chain branching reactions.

The growing chain end can react with dead polymer. It is presumed that it can either undergo a propagating reaction with double bonds in the polymer.



or it can undergo a chain transfer reaction such as:



In both cases undesirable branching occurs. These reactions are more likely to occur the greater the amount of polymer in the polymerizing system, and this is the reason why it is desirable to stop polymerization before it goes to completion.

The activation energy of these branching reactions, certainly of the latter type involving chain transfer[19], is higher than that of the normal propagating step of monomer addition. This means that the rate of the branching reactions is more dependent on temperature and the relative rates of the normal propagating reactions to the branching reactions increases with decreasing temperature. Therefore a more linear structure and better physical properties

can be obtained by reducing the polymerization temperature. This is the main reason for expecting that the use of reduction-activation in synthetic rubber manufacture will give improved products because it will permit the carrying out of the polymerization in reasonably short time schedules at much lower temperatures.

The presence of chain-transfer agents in the polymerizing system introduces another reaction that competes with the undesirable chain branching reactions and therefore tends to reduce the latter. They are more effective for this purpose, the greater is the tendency for chain branching. Thus they are more effective the more polymer is present in the polymerizing systems, and in the German continuous processes the tendency was not to add all the chain-transfer agent at the first polymerization vessel but to inject part into one or several of the later autoclaves in the polymerization train.

The I.G. used diproxid (diisopropylxanthogen disulfide) as a chain transfer agent in their Buna-S manufacture, and in America the preferred agent for GR-S manufacture was dodecanethiol. Our experience was that addition of either of these gives rubbers of improved plasticity, but also with poorer resilience, and better effects are produced by the use of higher concentrations of a less active chain-transfer agent, such as carbon tetrachloride. This is particularly so with butadiene and methyl methacrylate interpolymers[20].

The increase in plasticity on adding chain-transfer agents is, as pointed out previously, due to reduction in molecular weight and branching, but this is achieved at the expense of increasing the lower molecular-weight fractions in the rubber. This results in a decrease in resilience of the final vulcanized rubber because there are a larger number of free polymer ends to be pulled through the vulcanized structure on deformation.

It has been possible to deal with only the more important aspects, and perhaps the picture drawn has been oversimplified, but it is clear that considerable advances have been made during the last few years in our fundamental knowledge of the processes for making diene rubbers. Paralleling this there has been a continuous improvement in their technical properties, arising not only from improved polymerization procedure but also from adjustments that have been made in the compounding and vulcanization process. It is likely that this trend will continue, and the time will come when a descendant of the general-purpose synthetic rubber of the war years will evolve into a serious competitor with natural rubber in the abrasion resisting field, on a quality as well as on a cost basis.

REFERENCES

[1] Imperial Chemical Industries, Ltd., British patents 531,078 and 573,366.
[2] Imperial Chemical Industries, Ltd., British patents 476,244; 478,593; 485,941; 511,838; 514,912; 516,776; 520,022; 521,545; 568,561; and 573,529.
[3] Imperial Chemical Industries, Ltd., British patents 485,941 and 511,838.
[4] Imperial Chemical Industries, Ltd., British patent 521,545.
[5] Imperial Chemical Industries, Ltd., British patent 580,524.
[6] Morgan, *Trans. Faraday Soc.* **42**, 169 (1946).
[7] Bacon, *Trans. Faraday Soc.* **42**, 140 (1946).
[8] Imperial Chemical Industries, Ltd., British patent 573,366.
[9] Baxendale, Evans and Park, *Trans. Faraday Soc.* **42**, 155 (1946).
[10] Imperial Chemical Industries, Ltd., British patent application No. 24,072/45.
[11] Imperial Chemical Industries, Ltd., British patent 573,270.
[12] Imperial Chemical Industries, Ltd., British patent 578,846.
[13] Imperial Chemical Industries, Ltd., British patent 581,343.
[14] Weidlein, *Chem. Eng. News* **24**, 771 (1946).
[15] Alfrey and Goldfinger, *J. Chem. Physics* **12**, 205 (1944); Mayo and Lewis, *J. Am. Chem. Soc.* **66**, 1594 (1944); Wall, *J. Am. Chem. Soc.* **66**, 2050 (1944).
[16] Wall, *J. Am. Chem. Soc.* **66**, 2050 (1944).
[17] Semon, *Chem. Eng. News* **24**, 2900 (1946).
[18] Price and Read, *J. Polymer Research* **1**, 44 (1946).
[19] Mayo, *J. Am. Chem. Soc.* **65**, 2324 (1943).
[20] Imperial Chemical Industries, Ltd., British patent 511,838.

REFRACTOMETRIC DETERMINATION OF SECOND-ORDER TRANSITION TEMPERATURES IN POLYMERS. IV. BUTADIENE-ACRYLONITRILE COPOLYMERS *

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INTRODUCTION

A previous study of the low-temperature properties of a series of vulcanized butadiene-acrylonitrile copolymers[1] indicated an approximately linear relation between composition and brittle temperature. This study provides information relating low-temperature properties to copolymer composition for a series of industrially available butadiene-acrylonitrile copolymers of varying acrylonitrile content. The refractometric technique for determining second-order transition temperatures (T_m) as previously described[2] was used to determine T_m.

EXPERIMENTAL

The refractive index data were determined at temperatures down to −75° C with dry-ice refrigeration as previously described[2]. It is often difficult to mount butadiene-acrylonitrile copolymers so as to obtain a sharp line dividing the dark and light fields. The following procedure was used in this study. A 3-gram sample of the copolymer as supplied was pressed between sheets of aluminum foil at 100° C and 15,000 lbs. per sq. in. pressure for five minutes and cooled to 40° C under pressure. A Carver press with heated, water-cooled, 6-inch square platens was used. A piece of this film was clamped firmly but not too tightly between the prisms of an Abbé refractometer. Illumination by transmitted light was carefully adjusted to obtain a line which could be read to ±0.0003.

The Hycar-OR-15 copolymer was examined before and after milling. The sample was milled with cooling for 23 minutes on a 3 × 6-inch Stewart-Bolling rubber mill. The sample was pressed before mounting between the prisms. The values of T_m were −25° C unmilled and −26° C milled, from which it was concluded that a short milling does not appreciably alter T_m. The n_D^{26} value of 1.5187 was not changed by milling. At temperatures below 0° C, the n_D value of the milled sample was 0.0010 below that of the unmilled sample.

All but one of the polymers tested show a clear change of slope in the n_D-temperature data similar to that observed with other polymers[2]. The one polymer that did not show a clear break above −75° C may have contained sufficient low-molecular material to obscure the break. Another sample of the same copolymer showed the break.

Brittle temperature (T_b) measurements were made according to the technique previously described[3]. The copolymers were milled 30 minutes and molded in 0.5 × 0.125 × 1.5-inch test strips. Six or eight determinations were made at ±2° C of T_b to locate T_b within ±1° C.

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RESULTS AND DISCUSSION

The second-order transition temperature observed for the butadiene-acrylonitrile copolymers are listed in Table I and plotted in Figure 1. These data show a linear relation between T_m and acrylonitrile content within experimental error. The average deviation from the line as drawn is less than ±2° C, comparable with the accuracy of the determination of T_m, and the maximum deviation is from −5 to +3° C.

TABLE I

TRANSITION POINT DATA FOR BUTADIENE-ACRYLONITRILE COPOLYMERS

Copolymer	Acrylonitrile (%[a])	Nitrogen (%[b])	T_m (° C)	T_b (° C[c])	Source[d]
Perbunan-18	20.1	5.31	−56	−55	Enjay Company, Inc.
Perbunan-26NS60	28.6	7.55	−46	−46	Enjay Company, Inc.
Perbunan-35NS90	36.6	9.66	−34	−26.5	Enjay Company, Inc.
Hycar-OR-25	32.8	8.66	−37	−33	The B. F. Goodrich Chemical Co.
Hycar-OR-15	39.0	10.3	−26	−23	The B. F. Goodrich Chemical Co.
Butaprene-NF-NSP75	22.4	5.91	−52[e]	−49.5	Xylos Rubber Co.
Butaprene-NL	30.2	7.97	−41	−38	Xylos Rubber Co.
Butaprene-NL-NSP84	26.2	6.91	−50	−47	Xylos Rubber Co.
Butaprene-NAA	33.4	8.81	−39	−29	Xylos Rubber Co.
Butaprene-NXM	39.1	10.3	−33	−26	Xylos Rubber Co.
Butaprene-20-90	52.0	13.7	−16	−16.5	Xylos Rubber Co.
Chemigum-N4NS	30.8	8.13	−43	−35.5	Goodyear Tire & Rubber Co.
Chemigum-N3	39.5	10.4	−32	−26.5	Goodyear Tire & Rubber Co.
Chemigum-N3NS	39.7	10.6	−27	−24.5	Goodyear Tire & Rubber Co.

[a] Based on nitrogen analysis. With one exception (Butaprene-NL), these values are within 3 per cent of the values supplied by manufacturer.
[b] Value from Kjeldahl nitrogen analysis in this laboratory using procedure of Cole and Parks.[5]
[c] Determined by method of Selker, Winspear, and Kemp[3].
[d] The authors thank the various firms listed for generously providing samples and data.
[e] Another sample showed no break in n_D-temperature curve above −75° C.

Extrapolation to 100 per cent polybutadiene gives a value of −80° C. This is in fair agreement with the reported[4] value of −85° C for the brittle point of emulsion-polymerized polybutadiene as determined on vulcanized stock. Extrapolation to 100 per cent acrylonitrile gives a value of +52° C. This value compared with T_m values of crystalline polymers suggests a similarity of Nylon, T_m 47° C, rather than Saran, T_m −17° C.

For these polymers, the refractive index changes 0.00028–0.00034 unit per degree of centigrade above T_m, and 0.00020–0.00008 below T_m. These changes, summarized in Table II, show a possible relation between Δn and acrylonitrile content.

Comparison of the transition and brittle points of the unvulcanized butadiene-acrylonitrile copolymers reported here with the brittle point values for vulcanized copolymers previously reported[1] show that at 50 per cent acrylo-

TABLE II

REFRACTIVE INDEX INCREMENTS FOR COPOLYMERS ABOVE AND BELOW T_m

Acrylonitrile (%)	Δn/° C (above T_m)	Δn/° C (below T_m)	Acrylonitrile (%)	Δn/° C (above T_m)	Δn/° C (below T_m)
20.1	0.00034	0.00020	33.4	0.00032	0.00012
22.4	0.00034	0.00023	36.6	0.00033	0.00011
28.6	0.00033	0.00015	39.1	0.00030	0.00013
30.2	0.00033	0.00013	39.0	0.00033	0.00020
30.8	0.00032	0.00011	39.5	0.00031	0.00009
32.8	0.00034	0.00011	52.0	0.00028	0.00008

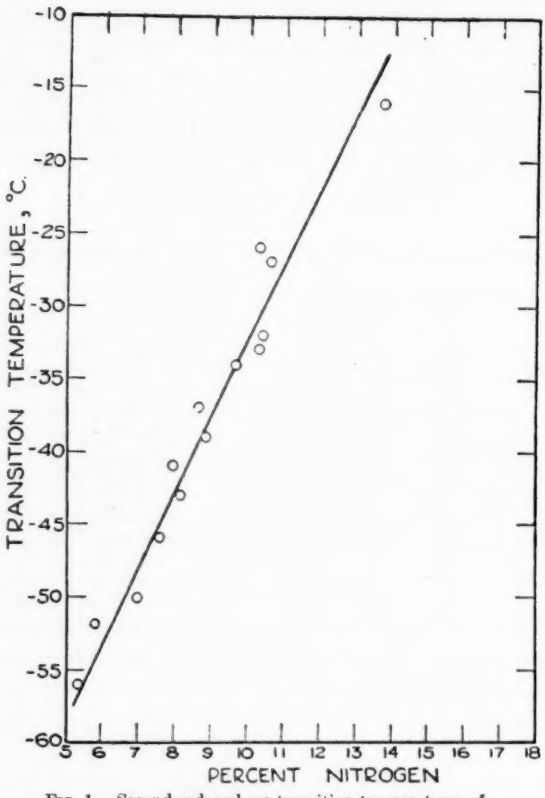

FIG. 1.—Second-order phase transition temperatures of acrylonitrile-butadiene elastomers.

nitrile, at which point all three values lie within one degree centigrade, vulcanization produces little if any change in brittle point. At concentrations of 20 and 30 per cent acrylonitrile, the brittle point is 5–8° C higher; the transition point is 6–13° C higher after vulcanization.

SYNOPSIS

The second-order transition temperatures (T_m) for fourteen commercially available butadiene-acrylonitrile copolymers with 18–50 per cent acrylonitrile have been determined refractometrically and found to be somewhat lower than the corresponding brittle temperatures (T_b). The data show a linear relation between T_m and acrylonitrile content.

ACKNOWLEDGMENT

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REFERENCES

[1] Border and Juve, *Ind. Eng. Chem.* **38**, 1066 (1946); RUBBER CHEM. TECH. **20**, 515 (1947).
[2] Wiley and Brauer, *J. Polymer Sci.* **3**, 455, 647 (1948).
[3] Selker, Winspear and Kemp, *Ind. Eng. Chem.* **34**, 157 (1942).
[4] Juve, Goff, Schroeder, Meyer, and Brooks, *Ind. Eng. Chem.* **39**, 1490 (1947).
[5] Cole and Parks, *Ind. Eng. Chem. Anal. Ed.* **18**, 61 (1946).

PROCESS PROBLEMS IN LOW-TEMPERATURE EMULSION POLYMERIZATION *

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The Government-sponsored synthetic rubber industry was originally established as a national defense measure. Its principal task was to provide a domestic supply of general purpose elastomer which would serve as a replacement for natural rubber. The standard GR-S process which was selected for the manufacture of this polymer gave a product recognized to be somewhat deficient in certain properties[1]. During the last four years there has been a concerted effort to develop improved elastomers which would equal or excel natural rubber in performance. Recently it has been shown that a greatly improved butadiene-styrene copolymer can be prepared by conducting polymerizations at temperatures considerably lower than the GR-S reaction level of 122° F. The low-temperature copolymers, which are rapidly progressing from pilot plant development to full scale production, show higher tensile strengths at both normal and elevated temperatures, better resistance to cracking, lower heat build-up, improved processability, and much improved tire treadwear, compared to standard GR-S[2]. Activation of the polymerization by special recipes is required.

In view of rapidly increasing interest in these new high quality products and expanded production, it is of interest to consider some of the chemical engineering problems involved in their manufacture. Standard GR-S is made at 122° F by polymerizing a 71/29 weight mixture of butadiene and styrene emulsified with soap in water[3], whereas the low temperature polymers are made in much the same way except that the temperatures range from 0° to 50° F. Emulsion polymerization at low temperatures brings up several major problems, none of which is presently involved in the manufacture of GR-S. These are: (1) the use of special activated recipes, (2) the refrigeration of polymerization equipment, and (3) the use of antifreezes.

In estimating the refrigeration requirements, overall heat transfer coefficients, reaction rates, heat of polymerization, and coolant compositions must be taken into consideration. Investigation of latex viscosity is also pertinent because of its influence on heat transfer. Where polymerization temperatures approach or go below the freezing point of water, the use of an antifreeze for the aqueous emulsion is involved. Recovery of this antifreeze from latex complicates the usual GR-S latex stripping operation, but is necessary to make the low-temperature process economically feasible.

Pilot plant investigations related to each of the above process problems have been carried out by the Phillips Petroleum Company during several years of development work. A general discussion of the low-temperature emulsion polymerization process which is based on this experience is presented in this article.

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ACTIVATION OF POLYMERIZATION RATES AT LOW TEMPERATURES

If the standard GR-S recipe were employed in the production of low temperature polymers, extremely long reaction times would be encountered. For example, although the normal time at 122° F is about 12 hours to 77 per cent conversions[3], it has been observed that approximately 25 to 65 hours would be required at 104° and 86° F, respectively. Polymerizations at lower temperatures would be even more impractical. Therefore, to manufacture low-temperature polymer at reasonable production rates, a reaction time approaching that of GR-S had to be established.

To accomplish this objective, considerable research was devoted to the development of special activated recipes which gave reaction times in the desired range. In general, a 12 to 18 hour reaction to 60 to 75 per cent conversion was considered satisfactory for plant-scale operations. Systems which resulted in relatively uniform rates of reaction throughout the polymerization were of particular interest from heat transfer considerations. In such reactions the maximum temperature differential required between the jacket and batch would be expected to be smaller than in runs where the rate of polymer formation (and rate of heat evolution) increases sharply during the course of the reaction.

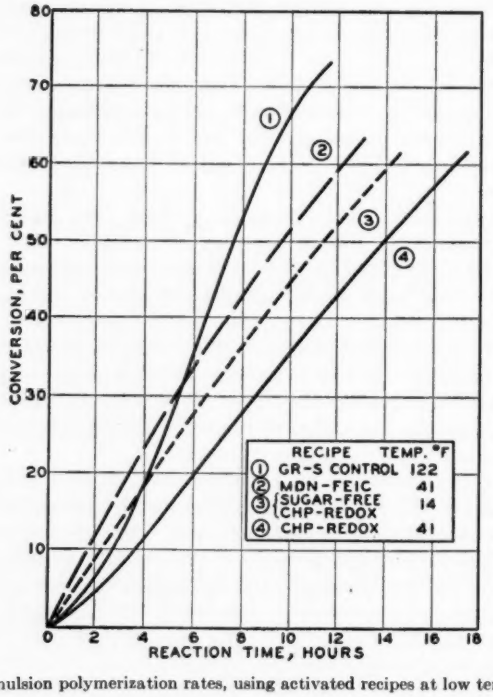

FIG. 1.—Emulsion polymerization rates, using activated recipes at low temperatures.

Typical time-conversion curves for several activated recipes, which were developed and eventually used by Phillips in the pilot plant production of low temperature polymers for tire tests, are given in Figure 1. The standard GR-S curve is included for comparison. Approximate compositions of the recipes involved are summarized in Table I.

TABLE I

ACTIVATED RECIPES FOR LOW TEMPERATURE EMULSION POLYMERIZATIONS

	MDN-feic recipe[1]	CHP-redox recipe[2]	Sugar-free CHP-redox recipe[3]	Standard GR-S
Reaction Temperature (° F)	41	41	14	122
	Recipe Parts by Weight			
Water	180	180	180–250	180
Methanol	—	—	16–25%[4]	—
Butadiene	70	72	70	72
Styrene	30	28	30	28
Emulsifier	4.7	4.7	5.0	4.3
Modifier	0.2–0.4	0.1–0.3	0–0.2	0.3
Catalyst	0.3	0.15	0.2	0.2
Activator	0.4	3.8	0.7	—
Electrolyte	0.6	0.6	0–0.4	—

[1] Diazothio ether-ferricyanide activation. [2] Iron pyrophosphate, sugar, cumene hydroperoxide system. [3] Sugar-free variation of 41° F CHP-redox system. [4] Percentage of total aqueous phase.

The relatively uniform reaction rates of the activated systems are apparent from the curves in Figure 1. In comparison, it is evident that GR-S polymerizes at a rather slow rate at the start, but then undergoes a marked increase in reaction rate beyond ten per cent conversion. The maximum rate seems to occur during a period of high latex viscosity (about 40 to 50 per cent conversion), where it has been observed[4] that heat transfer characteristics are ordinarily poorest. As a consequence, the maximum amount of cooling during GR-S runs must be provided when the jacket temperature is at a minimum. By contrast, the activated systems at 41° and 14° F show maximum rates early in the polymerization cycle, when latex viscosity is lowest and heat transfer conditions are more favorable.

HEAT TRANSFER CONSIDERATIONS

The exothermic heat of reaction during polymerization of GR-S is removed by circulating ordinary cooling water through the reactor jacket. When polymerizations are conducted at low temperatures, a special refrigerated coolant system must be installed. Before the capacity of such a refrigeration system can be calculated for a low temperature polymer production unit, several variables must be fixed. These are: (a) actual polymerization temperature; (b) available heat transfer area; (c) rate of heat evolution (average and maximum); (d) overall heat transfer coefficient, and (e) differential between batch and jacket temperatures.

For any particular system, the reaction temperature (a) and transfer area (b) are usually constant and readily established. Heat evolved in the polymerizer (c), which must be removed by the refrigerated coolant, is composed of heat of polymerization plus heat imparted by the agitator. The latter value has been determined experimentally as the difference between power required by the agitator during reaction and the no-load power demand. Heat load due to polymerization was based in the pilot plant studies on the rate of polymer formation and an estimated heat of polymerization (ΔH_p). Typical polymerization rates observed in low-temperature runs have already been described in the foregoing section. The selection of an average value for ΔH_p will be discussed later in this section. In the absence of data on overall

heat transfer coefficients (d) at low temperatures, experimental values were determined by the pilot plant. This work is also summarized later in this section.

After data for the first four points outlined above have been established, the required overall temperature differential (Δt) between coolant and batch (e) can be calculated from the general heat transfer equation:

$$q = UA\Delta t \tag{1}$$

or

$$q = Q_p + Q_a = (\Delta H_p)(W)/\theta + Q_a = UA\Delta t \tag{2}$$

where

q = heat transferred, B.t.u./hr.
Q_p = polymerization heat evolved, B.t.u./hr.
Q_a = heat of agitation, B.t.u./hr.
W/θ = weight of polymer produced, lbs./hr.
ΔH_p = heat of polymerization, B.t.u./lb.
U = overall heat transfer coefficient, B.t.u./(hr.) (sq. ft.) (° F).
A = area of cooling surface, sq. ft.
Δt = temperature differential (° F).

Then, using total heat load and indicated Δt, refrigeration needs for a specific polymerization process can be readily estimated. Examples of such calculations are presented in another section of this paper, following the discussion of pertinent heat data.

Heat of polymerization.—As previously described, the heat evolved during polymerization was calculated in pilot-plant tests from the rate of polymer formation (W/θ) and the heat of polymerization (ΔH_p). Selection of an average figure for ΔH_p was difficult, since a wide range of experimental and theoretical values were available. Following an analysis of all data, which took into consideration the fact that ΔH_p varies with the combining ratio of butadiene and styrene, it was estimated that 550 B.t.u. per lb. would be a reasonable average value for calculations. Even though the instantaneous heat of reaction may vary from this figure by ±50 B.t.u. per lb. during polymerization, the possible error amounts to less than ten per cent. This was eventually found to be accurate enough to show differences in the heat transfer characteristics at various temperature levels.

It should be mentioned in passing that the 550 B.t.u. per lb. value was selected on the basis of a combined styrene content in the polymer of about 23 to 24 per cent by weight. Polymers prepared at 41° and 14° F by Phillips have shown roughly 22 to 25 per cent styrene, depending on the butadiene-styrene charge ratio used. Currently GR-S averages about 23.5 per cent styrene[4].

As a check on the assumed value of ΔH_p the heat of polymerization for a 76/24 butadiene-styrene copolymer was calculated very roughly from heats of polymerization reported for butadiene[5] (19.0 k. cal. per mole) and styrene[6] (17.4 k. cal. per mole). A value of 554 B.t.u. per lb. was obtained which agrees very well with the value assumed in this study.

Heat transfer coefficients.—Overall heat transfer coefficients for the low temperature systems were calculated from pilot plant data on polymerizations carried out in a 260-gallon, glass-lined, jacketed vessel. Mixing was provided by a three-blade impeller agitator running at 100 r.p.m. The unit was equipped with a single baffle to prevent vortex formation. Heat transfer surface amounted to 39 to 41 square feet, depending on the volume of charge involved.

Heat removed by the jacket coolant was determined from the total heat of agitation and the heat due to polymer formation, as previously discussed. In all runs the heat of agitation (Q_a), based on power readings, was assumed to be 1000 B.t.u. per hr. Some slight variation from this value was noted in different recipes, and at low and high conversions in the same run, but the differences were found to represent only insignificant errors in final U values.

The average temperature differential between batch and jacket for any period of time was obtained by graphically integrating the area between the recorded batch and jacket temperature curves. Jacket temperature was taken as the average of inlet and outlet readings. Experimental results are discussed below.

(1) *122° F standard GR-S system.*—To compare heat transfer characteristics obtained in the 260-gallon pilot plant reactor to reported[4] standard plant data, several GR-S control batches were made at 122° F. U values at increasing conversions in these runs were calculated by Equation (2) in the following manner:

Period in run	5 to 6 hours
Conversion rise per hour	34.9 − 26.0 = 8.9%
Average conversion for period	(34.9 + 26.0)/2 = 30.5
ΔT	12.0° F.
Heat of agitation, Q_a	1000 B.t.u./hr.
Jacket area, A	39 sq. ft.
Monomer charge	550 pounds
ΔH_p	550 B.t.u./lb.

$$q = (\Delta H_p)(W)/\theta + Q_a = UA\Delta t$$

$$U = \frac{(0.089)(550)(550) + 1000}{(39)(12.0)}$$

U = 59.7 B.t.u./(hr.)(sq. ft.)(° F) at 30.5% conversion

Data for individual batches are summarized in Table II and plotted in Figure 2. Typical results[4] for a 3750-gallon plant batch are also included for comparison.

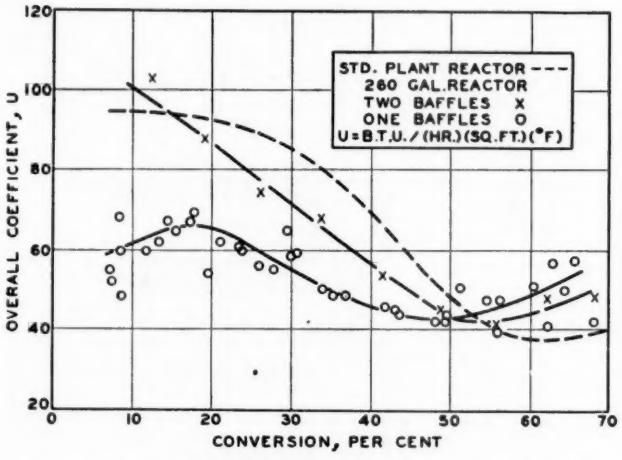

FIG. 2.—Overall heat transfer coefficients for GR-S recipe at 122° F.

TABLE II

VARIATION OF OVERALL HEAT TRANSFER COEFFICIENT WITH CONVERSION IN GR-S POLYMERIZATION AT 122° F

U = B.t.u./(hr.)(sq. ft.)(° F)

Standard plant reactor (4)		260 Gallon pilot plant reactor											
		R-3 (2 baffles)		R-7		R-12		R-15 (one baffle)		R-16		R-20	
% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U
10	95	12.0	103.0	3.0	60.1	8.4	60.0	7.5	52.0	8.2	68.5	8.5	48.3
20	94	18.9	88.2	7.0	55.3	15.1	65.7	13.3	62.7	17.5	69.4	14.4	67.4
30	86	25.9	74.2	11.6	60.3	23.5	60.5	19.4	54.4	29.4	65.1	20.8	62.1
40	70	33.5	67.8	17.2	67.4	30.5	59.4	26.1	56.2	42.9	45.5	27.7	55.3
50	48	41.4	54.1	23.3	61.1	39.4	46.0	34.0	50.8	—	—	35.3	48.9
60	37	48.8	45.0	29.9	58.9	48.2	42.9	41.9	46.0	—	—	43.4	53.2
70	40	55.6	41.9	36.7	48.9	56.0	40.0	49.5	43.9	—	—	51.2	51.1
—	—	62.2	47.8	43.3	44.6	62.5	41.5	56.4	48.1	—	—	64.5	50.3
—	—	68.0	48.2	49.4	42.3	68.1	42.1	62.9	57.6	—	—	69.0	42.7
—	—	72.4	45.3	54.8	47.8	—	—	—	—	—	—	—	—
—	—	—	—	60.6	51.9	—	—	—	—	—	—	—	—
—	—	—	—	65.7	58.1	—	—	—	—	—	—	—	—

In the first 260-gallon run (*R3*) where two baffles were present, the pilot plant *U* values closely approached the standard curve. A single baffle was used in all subsequent runs at 122° F or lower to reduce turbulence, which was observed to interfere with modification of the polymer at 122° F. As a consequence of reduced baffling, *U* values were considerably lower early in the run. Beyond 50 per cent conversion, the results were essentially identical for both types of baffling.

(2) *41° F activated systems.*—The two activated recipes used at 41° F gave slightly different heat transfer characteristics, *U* values being somewhat lower at all conversions for the MDN-feic system. This was attributed to higher latex viscosity, which in turn appeared to be controlled by the lower amount of water-soluble activator ingredients present. In Table I, it is seen that the MDN-feic system contains considerably less activator than the CHP-redox recipe.

Average *U* values for 41° F runs summarized in Table III are plotted against conversion in Figure 3. The minimum overall heat transfer coefficient with the CHP-redox recipe is about 38 B.t.u./(hr.) (sq. ft.) (° F), which is only slightly less than the minimum observed in the 122° F GR-S system.

(3) *14° F activated systems.*—At 14° F overall heat transfer coefficients were determined for several variations in the sugar-free CHP-redox polymerization recipe to establish which system gave the best results. The recipes used in the initial pilot plant work contained 180 parts of 16.7 per cent methanol. Latex was observed to be rather viscous, and freezing on the wall occurred when

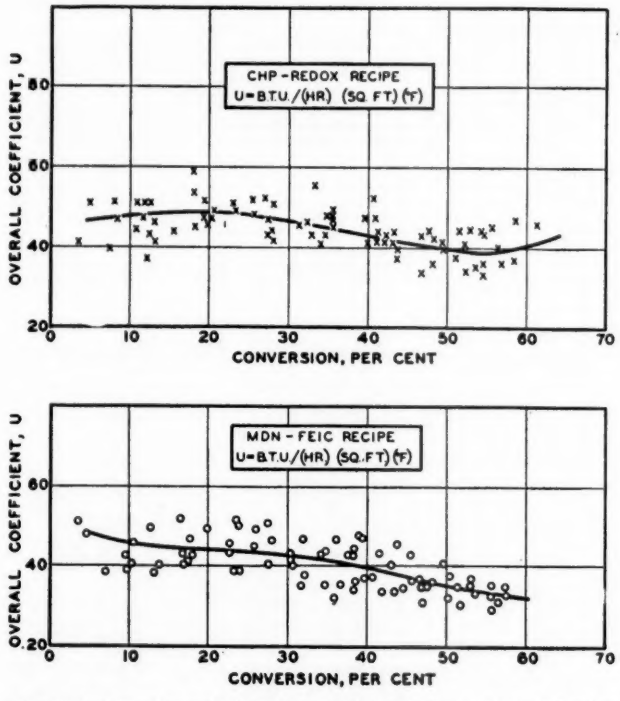

FIG. 3.—Overall heat transfer coefficients for activated recipes at 41° F in 260-gallon reactor.

TABLE III

VARIATION OF OVERALL HEAT TRANSFER COEFFICIENT WITH CONVERSION IN POLYMERIZATIONS CONDUCTED AT 14° F IN 260-GALLON REACTOR

U = B.t.u./(hr.)(sq. ft.)(° F)

MDN-feic recipe

Run 37		Run 36		Run 35		Run 26		Run 25		Run 27		Run 30		Run 23		Run 22		Run 21	
% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U
16.8	43.5	9.6	42.7	19.3	40.9	7.0	38.8	3.4	58.9	4.4	48.3	3.3	51.3	18.0	43.0	2.7	52.0	13.0	38.8
22.7	44.7	22.6	45.4	25.6	45.3	13.8	40.6	16.6	52.2	16.1	49.8	10.5	46.8	27.3	52.0	9.6	39.7	23.2	39.0
32.2	38.2	27.7	51.7	30.8	43.5	27.9	41.2	23.5	51.3	25.7	49.8	17.5	47.6	41.8	43.6	17.2	41.3	31.6	35.8
35.8	32.3	36.2	47.5	35.0	35.6	37.6	43.6	30.7	42.2	30.4	40.3	23.6	50.8	46.7	36.3	23.8	39.1	36.8	36.0
39.6	37.8	41.0	38.6	38.5	34.9	47.1	35.7	34.6	44.3	34.3	43.6	32.0	47.7	51.6	35.7	29.5	33.8	42.0	34.4
44.2	46.9	45.9	36.5	43.8	34.0	55.8	36.4	38.5	43.2	40.3	42.5	39.5	47.7	56.8	31.8	38.6	37.1	46.9	35.4
49.7	41.6	53.8	33.6	50.7	33.1	—	—	45.5	43.5	50.0	32.7	44.6	35.6	—	—	48.3	36.6	51.6	31.1
56.0	33.2	—	—	55.8	29.9	—	—	53.5	38.1	58.0	35.2	50.7	38.1	—	—	58.0	34.0	56.0	29.7

CHP-redox recipe

Run 70		Run 79		Run 62		Run 61		Run 59		Run 57		Run 52		Run 42		Run 38		Run 39	
4.9	50.8	7.3	39.5	12.7	46.3	12.9	40.8	8.0	51.3	12.1	50.8	12.4	43.0	11.8	50.2	11.8	36.5	3.9	50.0
10.6	50.8	18.6	45.5	20.3	48.1	20.3	48.5	17.9	53.6	20.3	49.3	19.5	45.7	27.9	50.8	19.4	52.1	11.4	47.0
22.9	50.0	31.3	45.3	41.0	41.2	27.3	42.5	27.0	52.0	34.6	43.1	27.3	47.1	35.5	49.2	27.7	41.8	19.2	47.4
34.9	48.3	43.0	41.3	53.0	44.9	34.0	41.0	35.5	49.6	41.3	43.7	35.2	47.9	42.5	42.8	35.7	45.3	32.4	46.3
45.2	42.4	54.1	35.3	—	—	41.0	48.4	43.5	39.4	48.1	35.5	42.8	43.6	52.3	41.0	43.7	37.8	39.5	47.5
49.2	41.7	—	—	—	—	47.8	44.0	51.3	44.4	54.2	36.8	49.2	39.4	—	—	51.2	37.7	46.8	43.6
55.7	45.2	—	—	—	—	54.5	33.2	—	—	58.2	36.7	56.3	39.8	—	—	58.7	47.6	54.3	44.4

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jacket temperature went below 0° F. The presence of a frozen latex film was reflected in U values, which dropped from about 27 to 15 B.t.u./(hr.) (sq. ft.) (° F) during the last hour of reaction. A subsequent run containing more aqueous phase (200 parts of 16.7 per cent methanol solution) to reduce the viscosity required jacket temperatures below −5° F, because of an abnormally fast reaction rate. Freezing was even more pronounced in this case, and U values dropped to ten B.t.u./(hr.) (sq. ft.) (° F). Four more batches with the same recipe (Table IV, Runs R90, 93, 94, and 95), which averaged 17 hours to 60 per cent conversion and which were controlled with the jacket at −2° F or higher, indicated an average minimum U value of 21 B.t.u./(hr.) (sq. ft.) (° F) at 60 per cent conversion. The average U value *vs.* conversion curve based on these runs is given in Figure 4.

When rapid reactions were subsequently encountered with the recipe containing 200 parts of 16.7 per cent methanol in two runs (R96–97), resulting jacket temperatures of −8° to −10° F again led to freezing of latex. The average U value curve for these batches is shown in Figure 4 to drop to nine

TABLE IV

VARIATION OF OVERALL HEAT TRANSFER COEFFICIENT WITH CONVERSION IN POLYMERIZATIONS CONDUCTED AT 14° F IN 260-GALLON REACTOR

U = B.t.u./(hr.)(sq. ft.)(° F)

Aqueous phase: 200 parts 16.7% methanol

Run 90		Run 93		Run 94		Run 95		Run 96*		Run 97*	
% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U
10.4	27.4	9.0	40.0	6.0	30.5	18.1	34.7	15.0	37.0	10.0	27.2
18.7	28.5	12.6	35.9	13.5	32.4	32.0	28.0	22.7	34.5	18.1	30.4
27.5	27.9	22.1	31.8	23.0	32.5	49.6	24.0	33.4	32.1	27.3	29.3
36.1	23.8	30.7	26.7	31.9	28.4	57.3	22.6	42.6	30.6	38.3	24.3
45.2	23.3	38.4	23.8	39.6	24.4	—	—	48.8	12.4	47.0	13.8
52.7	19.7	45.3	22.6	45.9	25.7	—	—	52.3	10.1	54.1	10.1
57.4	20.9	55.2	23.0	51.2	22.1	—	—	55.2	9.0	58.1	6.8
—	—	59.0	20.0	55.8	22.8	—	—	59.0	10.0	—	—

Aqueous phase: 200 parts 18% methanol

Run 99									
% Conv.	7.0	14.1	24.3	34.7	44.5	52.5	56.8	—	
U	24.8	27.6	32.7	31.3	18.8	17.1	16.2	—	

Aqueous phase: 210 parts 18% methanol

Run 100									
% Conv.	4.4	14.4	24.1	32.6	43.3	51.7	55.4	57.3	
U	33.0	31.7	26.8	24.2	23.5	24.5	26.9	23.9	

Aqueous phase: 220 parts 18% methanol

Run 102		Run 104		Run 112		Run 114		Run 117		Run 118	
% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U	% Conv.	U
9.0	22.4	2.0	37.3	8.4	39.9	7.0	30.1	5.9	32.9	6.8	25.5
12.9	34.4	7.5	29.7	17.0	39.9	11.9	34.9	15.7	35.3	13.7	31.6
19.4	36.0	15.6	35.9	27.0	30.3	16.8	33.8	25.5	32.7	23.2	29.5
26.6	33.6	24.3	36.4	35.9	26.6	29.2	30.4	34.9	31.9	32.4	30.2
37.0	28.8	32.6	30.2	44.1	24.2	37.0	27.7	43.8	25.6	40.9	27.3
46.0	23.4	40.4	26.7	51.2	23.4	47.6	23.4	52.3	20.5	49.0	22.3
53.7	22.1	—	—	56.7	27.7	53.0	25.8	—	—	55.8	25.1
58.7	19.6	—	—	—	—	58.1	32.7	—	—	—	—

* Freezing occurred.

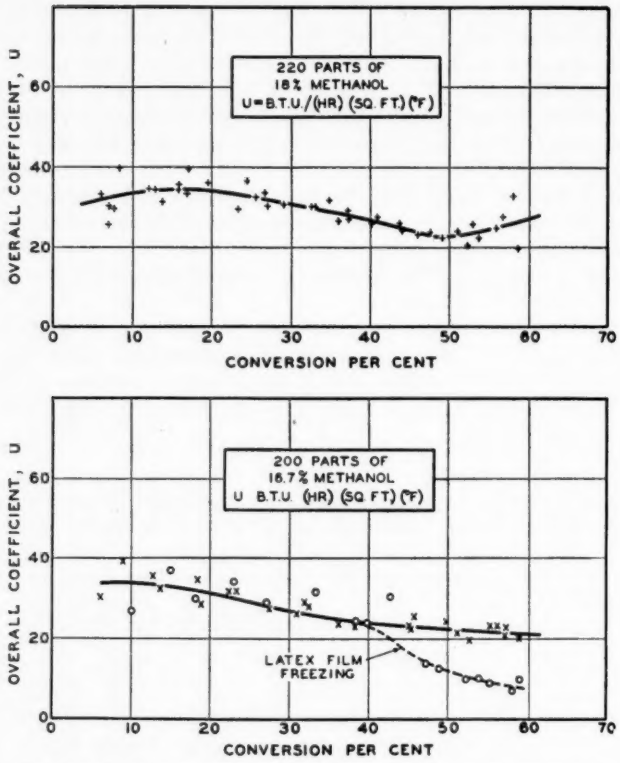

FIG. 4.—Overall heat transfer coefficients for sugar-free CHP-redox recipe at 14° F in 260-gallon reactor.

TABLE V

AVERAGE OVERALL HEAT TRANSFER COEFFICIENTS FOR LOW TEMPERATURE POLYMERIZATION SYSTEMS

U = B.t.u./(hr.)(sq. ft.)(° F)

	Minimum		U Values at % Conversion		
122° F Controls	U	at % Conv.	10	40	60
Standard Plant	38	60	95	70	38
260 gal. (2 baffle)	42	55	100	57	45
260 gal. (1 baffle)	43	50	62	46	49
41° F (260 gal.)					
MDN-feic	33	60	46	40	33
CHP-redox	39	54	48	43	40
14° F (260 gal.)					
Sugar-free CHP-redox (200 parts 16.7% CH_3OH)	21	60	34	24	21
Sugar-free CHP-redox (200 parts 18% CH_3OH)	23	50	34	27	27

B.t.u./(hr.) (sq. ft.) (° F). A layer of frozen latex one-half inch thick was noted in the reactor when these runs were discharged. Detailed data are listed in Table IV.

Increasing the methanol in the aqueous phase to 18 per cent in batch R99 still failed to maintain a suitable transfer coefficient in the fast 14° F runs.

Values approached 15 B.t.u./(hr.) (sq. ft.) (° F) at the end of the run. Since freezing was not encountered in this case, it was concluded that the poor heat transfer was due to high latex viscosity. To reduce viscosity, the aqueous phase was increased to 210 parts (R-100), and then to 220 parts (R-102) of 18 per cent methanol. The overall heat transfer coefficients were improved by this dilution, as shown by the average curve in Figure 4 for the system containing 220 parts of 18 per cent methanol.

(4) *Summary of overall coefficients.*—The variation of U with conversion for the systems which have been discussed above is summarized in the average curves of Figure 5. Typical data are given in Table V.

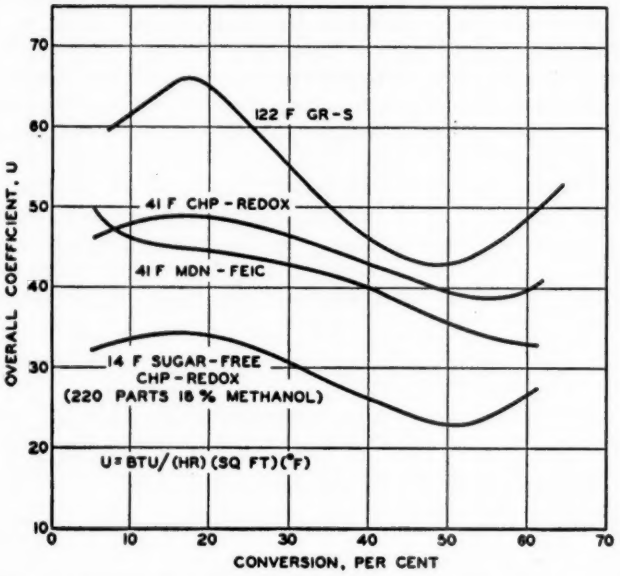

FIG. 5.—Effect of temperature and recipe on overall heat transfer coefficient in 260-gallon reactor.

Viscosity of latex.—It can be shown that fairly accurate heat transfer coefficients can be calculated for latex films on pipe walls by using the McAdams[7] equation for liquids in turbulent flow in round tubes:

$$\frac{hD}{k} = 0.023(DG/\mu_\infty)^{0.8}(C\mu_\infty/k)^n \tag{3}$$

where

h = film coefficient of heat transfer
D = inside diameter of pipe
k = thermal conductivity
G = mass velocity
μ_∞ = limiting viscosity
C = heat capacity
n = 0.3 for cooling

It is apparent from this equation that h may be expressed as a function of both G and μ_∞ as shown below:

$$h = f(G/\mu_\infty)^{0.8}(\mu_\infty)^{0.3} \tag{4}$$

$$h = f(G)^{0.8}(\mu_\infty)^{-0.5} \tag{5}$$

The simplified relationship (Equation 5) given above was applied to the analysis of the heat transfer problem in the agitated polymerization reactor. Two assumptions were made: first, that the overall heat transfer coefficient (U) is controlled primarily by the latex film; and second, that velocity of latex past the reactor wall does not vary appreciably because of constant speed agitation. This means that U should be influenced principally by changes in latex viscosity, and the higher viscosities encountered at low temperatures should, therefore, lead to poorer heat transfer coefficients.

On the basis of this reasoning, it was decided to obtain latex viscosity data for various recipes tested in the pilot plant at 14° F. Results were used in predicting changes in the U values. Unvented latex samples were withdrawn from the reactor into a precooled receiver held at about 0° to 10° F. Apparent viscosities were determined with a Brookfield Synchro-Lectric (rotating cylinder) viscometer. Since the rate of shear exerted by the constant speed rotating cylinder was relatively low, readings were estimated to be somewhere in the range between the limiting viscosity (μ_∞) and viscosity at zero shear, (μ_0), as discussed by Winding[8].

Winding has reported that μ_0 for GR-S latex at 68° F rises from 6.5 cp. at 20 per cent conversion to 32 cp. at 80 per cent. By contrast, μ_∞ is constant at 6.5 over the same conversion range. As latex temperature drops from 104° to 41° F, μ_∞ increases from 5.2 to only 9.3 cp. The higher values for μ_0 reflect the pseudoplastic character of unvented latex, which shows relatively high

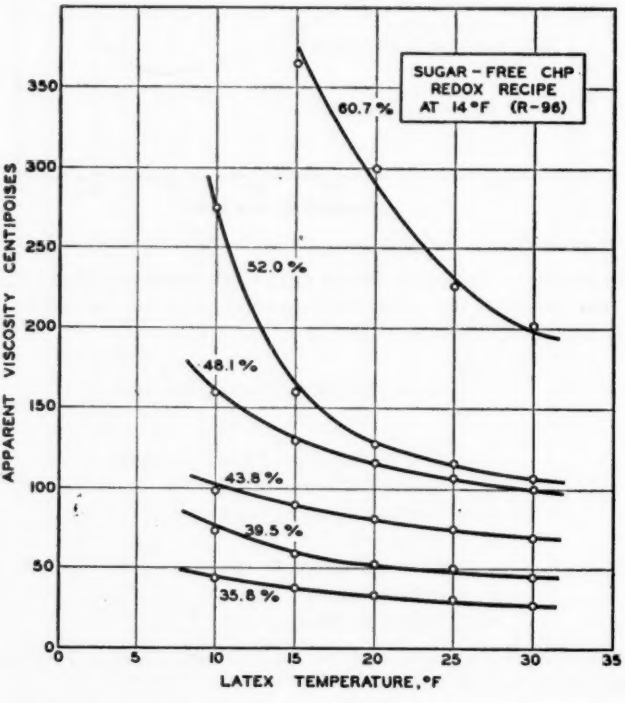

FIG. 6.—Variation of apparent viscosity of unvented latex with temperature and conversion.

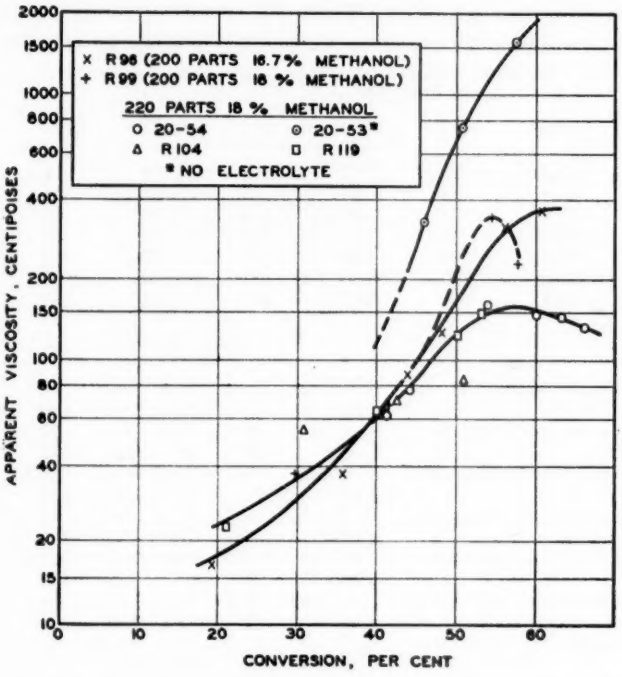

FIG. 7.—Variation in apparent viscosity of unvented latex with conversion at 14° F.

stresses for low rates of shear. Apparent viscosities measured during this program were considered to be more closely comparable to the μ_∞ data mentioned above.

Although the experimental values were only considered qualitative, they were sufficiently graphic to allow prediction of improvements in overall heat transfer coefficients. A series of typical curves showing the effect of temperature on latex viscosity at increasing conversion is shown in Figure 6 for 14° F run R96. Viscosity-conversion data for several different systems are plotted in Figure 7. Data are summarized in Table VI.

The remarkable effect on viscosity of omitting electrolyte from the system containing 220 parts of 18 per cent methanol in run 20–53 is clearly evident. Because of the high apparent viscosities and the expected low U values, no large scale work was conducted with this recipe. The high viscosity values for R96 and R97 (200 parts of 16.7 per cent methanol) at 50 to 60 per cent conversion (Figure 7) are reflected in the relatively low U values reported in the preceding section (Figure 4). The 260-gallon runs containing 220 parts of 18 per cent methanol which had lower viscosities (R104, R119), also had better coefficients (Figure 4). On the basis of these examples, it was concluded that the viscosity technique would be useful in evaluating the effect of such factors as the types and amounts of emulsifier, antifreeze or electrolyte on the overall heat transfer coefficients.

TABLE VI

APPARENT VISCOSITY OF LATEX POLYMERIZED AT 14° F
Variation with temperature at increasing conversion
Batch R96 (200 parts of 16.7% CH_3OH)

% Conv.	10° F	15° F	20° F	25° F	30° F
		(Viscosity in centiposes)			
19.3	19	17	15	13	11
35.8	43	38	35	32	28
39.5	73	60	54	49	45
43.8	99	89	82	75	69
48.1	160	130	117	107	99
52.0	275	160	127	116	105
60.7	—	367	300	252	203

Run No.	Type	Variation with conversion at 15° F					
R96	(200 parts 16.7% CH_3OH)	% Conv.	19.3	35.8	43.8	48.1	56.0	60.7
		μ cp.	17	38	89	130	320	367
R99	(200 parts 18% CH_3OH)	% Conv.	29.8	41.9	54.4	57.9	—	—
		μ cp.	38	68	350	235	—	—
R100	(210 parts 18% CH_3OH)	% Conv.	30.1	39.6	49.1	55.4	58.3	—
		μ cp.	71	75	93	125	185	—
R104	(220 parts 18% CH_3OH)	% Conv.	30.5	42.4	50.7	—	—	—
		μ cp.	55	70	85	—	—	—
R119	(220 parts 18% CH_3OH)	% Conv.	22.3	40.0	50.4	55.8	—	—
		μ cp.	24	65	125	150	—	—
20–54	(220 parts 18% CH_3OH)	% Conv.	41.1	44.1	53.9	59.8	63.0	66.0
		μ cp.	62	77	163	150	147	133
20–53*	(220 parts 18% CH_3OH)	% Conv.	45.7	50.4	57.0	—	—	—
		μ cp.	338	770	1600	—	—	—

* No electrolyte; all other runs contain 0.4 part electrolyte.

REFRIGERATION REQUIREMENTS FOR LOW TEMPERATURE POLYMERIZATIONS

Calculations for plant scale operation.—Using data developed in the preceding sections, calculations were made to determine refrigeration requirements for polymerizations conducted in the 3750-gallon standard GR-S plant reactors at 41° and 14° F. Total heat load in each case was based on operation of the 24 reactors available in a 30,000 ton per year standard plant. It was assumed that each reactor batch contained 8000 pounds of monomers, and was reacted to 60 per cent conversion. Reaction times at 41° and 14° F were established at about 17 and 14 hours, respectively, for the CHP-redox systems (see Figure 1). This corresponds to average rates of 3.5 and 4.3 per cent conversion per hour. Rates were only 3.3 and 3.6 per cent per hour at about 50 per cent conversion, where the minimum U values were observed. Minimum overall heat transfer coefficients at the two reaction temperatures were taken from Table V as 38 and 23 B.t.u./(hr.) (sq. ft.) (° F). Heat transfer area available in the reactors has been calculated as 270 square feet, while heat of agitation has been estimated[4] at roughly 15,000 B.t.u. per hr. The assumed heat of polymerization was again set at 550 B.t.u. per lb.

With the above information, the temperature differential between batch and jacket at the lowest U value was first calculated as follows from Equation 2:

$$(\Delta H_p)(W)/\theta + Q_a = UA\Delta t$$

At 41° F:

$$(550)(8000)(0.033) + 15{,}000 = 38(290)(\Delta t)$$

$$\Delta t = \frac{160{,}500}{11000} = 14.6° \text{ F}$$

At 14° F:

$$(550)(8000)(0.036) + 15{,}000 = 23(290)(\Delta t)$$

$$\Delta t = \frac{173{,}200}{6670} = 26° \text{ F}$$

These values indicate that reactions would require minimum jacket temperatures of

$$41\text{–}14.6 = 26.4 \text{ at } 41° \text{ F; and } + 14\text{–}26 = -12° \text{ F at } 14° \text{ F}$$

Having thus established the minimum coolant temperature, the total refrigeration capacity was estimated next. The following services were considered:

(1) Maintenance of jacket temperature sufficient to control reaction (removal of reactor heat load).
(2) Cooling of reactants to reaction temperature.
(3) Compensating for heat gain through insulation and mechanical action of coolant pumps, etc.

If reactions are 17 hours at 41° F, and one hour is allowed for charging and discharging, the total time cycle per reactor is 18 hours. At 14° F, the cycle would be 15 hours. In a 24 reactor plant, maximum daily heat load would be calculated as follows:

REACTOR HEAT LOAD

At 41° F: $\frac{24}{18} \times 24 = 32\text{–}17$ hr. batches per day

$$Q = 32[(8000)(0.035)(550) + 15000]17 = 91{,}800{,}000 \text{ B.t.u. per day}$$

At 14° F: $\frac{24}{15} \times 24 = 38.4\text{–}14$ hr. batches per day

$$Q = 38.4[(8000)(0.043)(550) + 15000]14 = 109{,}550{,}000 \text{ B.t.u. per day}$$

SENSIBLE HEAT OF CHARGE

Each reactor charge of roughly 3100 gallons must be reduced from about 80° F to the reaction temperature. Using an approximate specific heat of 0.8 and specific gravity of 0.9 (7.5 lbs. per gal.), cooling requirements involved are:

At 41° F:

$$32.0(3100)(7.5)(0.8)(80\text{–}41) = 23{,}220{,}000 \text{ B.t.u. per day}$$

At 14° F:

$$38.4(3100)(7.5)(0.8)(80\text{–}14) = 47{,}100{,}000 \text{ B.t.u. per day}$$

HEAT GAIN THROUGH INSULATION

During 41° F operation, with coolant at about 20° to 25° F, heat gain through insulation of reactors, coolant tanks and lines, and primary refrigera-

tion equipment has been estimated at 100,000 B.t.u. per hr., or 2,400,000 B.t.u. per day for ambient temperatures of 80° F. At 14° F, the gain would be 3,695,000 B.t.u. per day.

HEAT OF PUMPING

Coolant circulation pumps on reactor jackets and on the main feed to the evaporators would represent a total power load of about 200 h.p. Assuming that total power rating represents energy converted to heat, then 200 × 24 × 2546 equals a heat output of 12,250,000 B.t.u. per day, where 2546 B.t.u. is equivalent to one h.p.-hr. This estimated value was arbitrarily used for final refrigeration calculations at both 41° and 14° F.

TOTAL HEAT LOAD SUMMARY

	At 41° F	At 14° F
Rector heat load	91,800,000	109,500.000
Sensible heat of charge	23,220,000	47,100,000
Insulation heat gain	2,400,000	3,695,000
Heat of pumping	12,250,000	12,250,000
	129,670,000	172,545,000

Total refrigeration load based on the above values is equivalent to 450 tons at 41° F and 599 tons at 14° F, where 288,000 B.t.u. per day equals one ton of refrigeration. In the design of a refrigeration system, these ratings would have to be specified at the minimum coolant temperatures previously determined at 41° and 14° F; that is, at roughly 25° and −15° F, respectively.

The cooling loads calculated above could be reduced somewhat if heat exchange were provided between charge ingredients and discharged latex. Such an operation would be most feasible in a plant where polymerization is carried out continuously. Even then, it is anticipated that the maintenance of a satisfactory coefficient on the latex film side might pose a major problem. Fouling by precoagulum formation could reduce over-all heat transfer coefficients to a point where precooling would be inadequate at the normal rates of flow through the exchanger.

Phillips pilot plant refrigeration installation.—When the Phillips Petroleum Company rubber pilot plant was designed in 1942, a 20-ton mechanical refrigeration unit was specified to control polymerizations in a 260-gallon reactor at temperatures ranging from 0 to 150° F. The unit is described briefly at this point.

Propane is used as the primary refrigerant in the system, and 40 per cent aqueous methanol serves as the coolant which is circulated through the reactor jacket. Methanol is cooled by heat exchange with propane in process of being evaporated at constant pressure. Coolant temperatures out of the evaporator are regulated by automatic control of the propane pressure in the evaporator. Propane level in the unit is also maintained automatically by a liquid level controller. Propane vapor from the evaporator is compressed to 100 to 150 psig with a steam-driven Ingersoll-Rand engine. The vapor is then condensed at 90° to 100° F, liquid being accumulated in a 200-gallon storage tank.

The temperature of the coolant entering the reactor jacket is automatically controlled by blending proper volumes of refrigerated methanol from the propane evaporator and warm methanol from a steam-heated exchanger with the main recirculation stream. Methanol is stored in a 300-gallon surge tank, and is circulated to the reactor system by a Goulds centrifugal pump. The flow diagram for the system is shown in Figure 8.

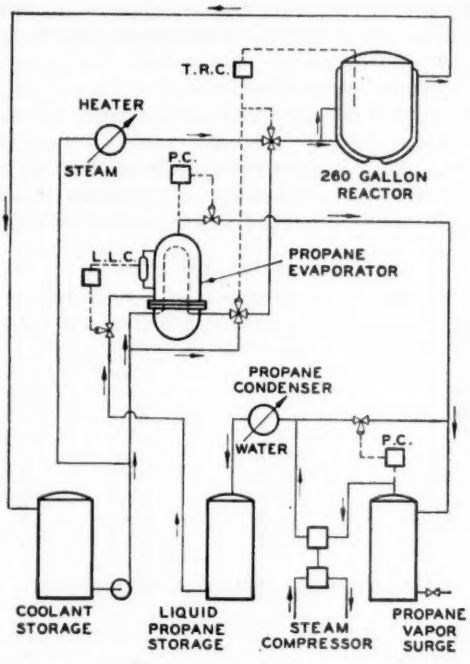

FIG. 8.—Refrigeration system for 260-gallon pilot plant reactor.

ANTIFREEZE REQUIREMENTS IN THE EMULSION

During the development of low-temperature polymers, batches were made at progressively lower temperatures as new activated polymerization recipes were perfected to give faster reaction rates. Eventually a point was reached where the problem of freezing latex had to be considered. Observations made in the 260-gallon pilot plant reactor indicated that 41° F polymerizations could be controlled with the coolant at 25° F, with no indication of freezing at the reactor wall. Even minimum reactor jacket temperatures as low as 20° F could be tolerated for periods of 0.5 to 1.5 hours. However, these minimum values were encountered only at low conversions, where the latex film viscosity was relatively low. At higher conversions, where latex becomes more viscous, it is anticipated that freezing might eventually occur if the jacket were held much below 20° F. It is assumed that the electrolytes and other water-soluble compounds contained in the special activated recipes (Table I) are responsible for the depression in the normal freezing point of water which has been observed in these systems.

Pronounced freezing was actually noted in one abnormally fast 41° F batch which required coolant below 15° F for two hours early in the run. The layer of frozen latex which deposited on the reactor wall was about $\frac{3}{4}$ inch thick. Its presence was reflected in very poor heat transfer coefficients.

On the basis of the observations outlined above, it was concluded that jacket temperatures of 20° to 25° F could be safely tolerated in the activated polymerization systems containing no special antifreeze. This temperature limits the maximum temperature differential between jacket and batch to 16° to 21° F.

When emulsion polymerizations were conducted at temperatures in the range of 0° to 35° F, a special antifreeze compound had to be added to the reaction recipe to prevent freezing. Laboratory investigation of numerous materials to serve as emulsion antifreezes showed that ethyleneglycol, glycerol, methanol, dioxane, methylcellosolve and diethyleneglycol met one of the principal qualifications; that is, they did not seriously retard the polymerization when present in the aqueous phase to the extent of 20 to 25 per cent. Ethanol and acetone were pronounced inhibitors. Typical reaction data showing the effect of antifreeze in two different activated recipes are given in Table VII.

TABLE VII

EFFECT OF VARIOUS ANTIFREEZES OF POLYMERIZATION RATE

(Sugar-free CHP-redox recipe, 140 water/140 antifreeze)

Type antifreeze	Boiling pt. (° C)	% Conversion at 59° F after		
		4 hrs.	8 hrs.	24 hrs.
Control, 180 H_2O	—	35.1	64.5	92.7
Methanol	64.7	21.9	43.4	85.8
Dioxane	101.4	0.2	1.5	54.9
Methylcellosolve	124.3	22.8	42.6	82.0
Ethyleneglycol	197.2	41.3	74.0	—
Diethyleneglycol	245.0	37.3	65.0	—
Glycerol	290.0	42.7	79.0	—

(MDN-feic recipe, 200 water/50 antifreeze)

Type antifreeze	Boiling pt. (° C)	% Conversion at 41° F after		
		4 hrs.	7.5 hrs.	24 hrs.
Control, 250 H_2O	—	56.4	69.9	72.5
Acetone	56.1	3.9	—	24.5
Methanol	64.7	17.3	31.1	61.6
Ethanol	78.3	0.1	—	3.5
Dioxane	101.4	13.4	29.5	59.6
Ethyleneglycol	197.2	59.4	75.1	83.9
Glycerol*	290.0	52.4	65.5	—

* 175 H_2O/75 glycerol.

Although glycol and glycerol actually accelerated the polymerizations, they were not considered practical antifreezes on account of their high boiling points. Recovery of these compounds from the latex by distillation, stripping or extraction if at all possible, would constitute a major problem. Methanol, on the other hand, had one of the lowest boiling points of the materials evaluated and preliminary tests demonstrated that it could be recovered readily by steam stripping or distilling from the latex. For this reason, and despite the fact that it was a slight retarder, methanol was selected as the standard antifreeze. Methanol was also desirable from a cost standpoint, since it is cheaper than glycols and much less is required to give equivalent depression of freezing. The latter point is apparent from the data given in Table VIII. Another advantage was that latices containing methanol were much less viscous.

In preliminary investigations at 14° F, the water phase in polymerizations was first adjusted to 16.7 per cent methanol (150 water/30 methanol). By interpolating from data in Table VIII, a freezing point of roughly 9° F (flow point 5° F) is indicated for this mixture. However, electrolytes in the recipe depress the freezing point further, apparently to the same extent previously observed in the 41° F system. Latex based on the 150/30 recipe did not freeze upon the 260-gallon reactor walls until coolant temperatures of about 0° F were experienced.

Inspection of latex taken from one of the 14° F reactions showed that it was slushy at 0° F and a paste at −5° F. Since the latex was extremely viscous, the total aqueous phase was increased from 180 to 200 recipe parts. Latex in runs at this level did not freeze even when jacket temperature dropped to −2° F. However, freezing was observed in several rapid runs which called for coolant at −8° to −10° F, so the alcohol content was raised to 18.0 per cent. Simultaneously, the total water phase was increased to 220 parts to reduce latex viscosity even further. The resulting recipe, which was eventually used in the preparation of substantial quantities of 14° F polymer, gave no freezing with coolant temperatures at −10° F.

TABLE VIII

PROPERTIES OF AQUEOUS SOLUTIONS OF SEVERAL ANTIFREEZES[9]

	Ethyleneglycol		Methanol		Glycerol	
Weight per cent	F.P. (° F)	Flow point (° F)	F.P. (° F)	Flow point (° F)	F.P. (° F)	Flow point (° F)
15	—	—	13.1	+ 7.0	—	—
20	18.0	16.6	+ 2.8	− 1.1	22.5	15.8
25	—	—	− 6.2	−11.2	—	—
30	7.7	+ 6.8	−18.4	−10.2	16.3	+ 3.5
35	+ 1.2	− 2.4	−31.4	−40.0	7.5	− 2.0
40	− 7.8	−12.1	−43.6	−57.1	1.0	− 3.1
45	−16.0	−30.1	—	—	+ 0.4	− 4.0
50	−31.7	−47.4	—	—	− 6.5	−18.4
55	−43.0	−52.6	—	—	−17.5	−32.6
60	−50.8	−63.4	—	—	−29.2	−43.6

ANTIFREEZE IN THE COOLANT

In running standard GR-S polymerizations at 122° F, the heat of reaction is removed through the reactor jacket with ordinary cooling tower water at 70° to 110° F, depending on heat evolution rates and existing heat transfer coefficients. When low-temperature polymerizations are involved, water alone is an unsatisfactory coolant since subfreezing temperatures are ordinarily required. As in most refrigeration processes, a nonfreezing fluid must be used in the cooling system. This coolant must be able to withstand freezing at the temperature of the primary refrigerant (ammonia, Freon, propane, etc.). For example, if it is assumed that a 0° F polymerization requires coolant at −20° F, and refrigerant evaporates at −30° F to maintain this temperature, then a coolant which does not freeze at −30° F or lower is obviously required.

Proper concentrations in water of various standard antifreezes can be prescribed to meet the conditions of such a low temperature process. Calcium chloride, though the least expensive, may be corrosive under aerating conditions, and further might not be suitable for 0° F operation. Sodium chloride cannot be used below its eutectic point of −6.0° F. Methanol, which has been employed in pilot-plant operations for several years, is essentially noncorrosive, but more costly than calcium chloride. Glycols are even more expensive, higher concentrations are needed to give a desired freeze point, and solutions are more viscous, requiring extra power for pumping. In this last respect, calcium chloride and methanol solutions are practically equivalent. Isopropanol cannot be considered at temperatures approaching −30° F, since like glycols it requires higher concentrations and is considerably more viscous than methanol. It is fairly suitable at higher temperatures, however.

METHANOL ANTIFREEZE RECOVERY

When methanol is used as the antifreeze in low temperature emulsion polymerizations, there must be a provision in the process for recovering it from the latex, and recycling it in subsequent batches. These steps are obviously necessary if antifreeze costs are to be held to a minimum. Preliminary pilot-plant studies have indicated that essentially all methanol can be removed from latex during the same operations required to effect recovery of unreacted butadiene and styrene. A small amount of methanol is carried over during the venting of butadiene, while the major portion is taken over with the styrene during the steam stripping step.

Latex made in the pilot plant was stripped in a 12-inch diameter, perforated-plate Pyrex column maintained at 100 mm. Hg absolute pressure. This corresponded to a top temperature of 125° to 130° F. Pressure drop through the 10 plate column amounted to about 75 mm. Hg. Latex was charged at a rate of 1.0 to 1.7 g.p.m. and steam was adjusted to give steam to unreacted styrene weight ratios of 4 to 1 to 8 to 1. A ratio of about 4 to 1 is generally employed in large scale operations where no methanol is present. Greater amounts of steam appeared necessary in stripping low temperature latex to recover the methanol antifreeze.

Ternary system methanol-water-styrene.—Condensate from the stripping operation separates into two phases: an upper styrene layer saturated with methanol and water, and a lower aqueous methanol layer saturated with styrene. In conjunction with the problem of analyzing this condensate, the solubility diagram for the system styrene-methanol-water was determined. Mixtures of freshly distilled styrene and cp. methanol covering a large range of concentrations were titrated with distilled water to the first appearance of turbidity, which indicated the presence of a second phase. Samples were maintained in a constant temperature bath during titration. The equilibrium ternary compositions obtained in this manner define a solubility curve which divides the regions of one and two homogeneous liquid phases. Equilibrium data were established at both 15° and 25° C. Only a relatively small difference was noted between the two solubility curves. The curve obtained at 15° C is reproduced in Figure 9. Tie lines included in this diagram were obtained by allowing several heterogeneous ternary mixtures of known compositions to separate into conjugate layers and determining compositions of both phases.

Specific gravities of the conjugate ternary solutions originally used in defining the solubility curve at 15° C were measured at 25° C to permit a correlation between specific gravity and methanol content of the equilibrium solutions. The specific gravity curve is shown in Figure 10. It was used for analysis in the following manner. Styrene and aqueous methanol phases obtained during stripping were allowed to reach equilibrium at about 15° C and were then separated. Specific gravities of both phases were measured at 25° C and methanol contents were read from Figure 10. Locating these values on the proper portion of the equilibrium curve in Figure 9 gave the ternary composition of both phases. Tie lines between these ternary points fell into the existing family of lines previously established if the sample phases were in equilibrium. It was estimated that results obtained by this approximate method of analysis were only accurate to 0.5 to 1.0 per cent of methanol in either phase. Styrene determinations by bromine titration were used to check data obtained by the gravity-composition correlation.

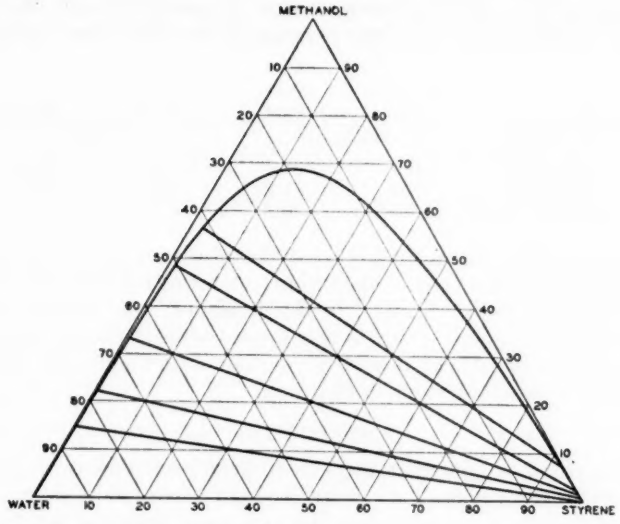

FIG. 9.—Ternary equilibrium diagram for system styrene-methanol-water at 15° C.

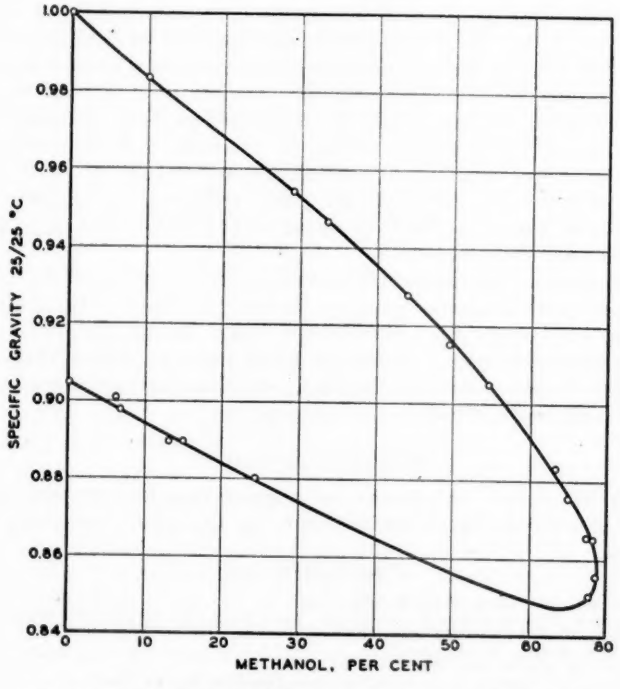

FIG. 10.—Specific gravity 25/25° C *vs.* methanol content of equilibrium mixtures of styrene-methanol-water prepared at 15° C.

Stripping results.—Average composition of methanol and styrene layers from a typical continuous stripping operation in the pilot plant were as follows:

	Aqueous phase	Styrene phase	Latex	
			Feed	Stripped
Compound	Weight %		Weight %	
Styrene	0.5	98.7	3.3	0.3
Methanol	37.0	1.2	13.0	0.2
Water	62.5	0.1	—	—

Depending on the steam rates, the methanol content of the aqueous phase varies from 30 to 45 per cent. Since this is substantially greater than the 18 to 25 per cent which may be used in the emulsion, it is evident that the recovered methanol can be recycled to the process without further concentration. The small amount of styrene present in methanol and methanol in recovered styrene can be compensated for in charging,

SUMMARY

When emulsion polymerization of butadiene and styrene is conducted at temperatures in the range of 0° to 41° F, high elastomers possessing greatly improved properties are produced. However, low temperature operation involves several major process problems not encountered in the manufacture of standard GR-S at 122° F. These are the use of activated reaction recipes, the refrigeration of polymerization equipment, and the use of emulsion antifreezes.

Redox-type activated systems which have been developed for low temperature runs in the pilot plant result in reaction rates approaching those of normal GR-S even at 14° F. Heat transfer characteristics of typical activated recipes at 41° and 14° F have been investigated in a 260-gallon reactor and compared to similar results for GR-S at 122° F. Variation in overall heat transfer coefficients with conversion has been established at each temperature. Minimum U values of 43, 39 and 23 B.t.u./(hr.) (sq. ft.) (° F) were obtained at 50 to 55 per cent conversion in polymerizations run at 122°, 41° and 14° F.

Using experimental heat transfer data, refrigeration requirements for a standard 30,000 ton/year plant operating at 41° F and 14° F are calculated as 450 and 599 tons, respectively.

When emulsion polymerizations are conducted at about 0° to 35° F, special antifreezes such as methanol must be included in the reactionrecipe. Methanol is recovered from latex during the usual stream stripping of latex to remove unreacted styrene. A ternary equilibrium solubility diagram for the system styrene-methanol-water has been established to facilitate analysis of the two-phase condensate obtained during stripping.

ACKNOWLEDGMENT

The author wishes to express his appreciation to members of the pilot plant staff and the Research Department who assisted in collecting the experimental data.

REFERENCES

[1] Soday, *Trans. Am. Inst. Chem. Engrs.* **42**, 647 (1946).
[2] Schulze, Reynolds, Fryling, Sperberg, and Troyan, *India Rubber World*, **117**, 739 (1948).
[3] Dunbrook, *India Rubber World* **117**, 203 (1947).
[4] Pahl, *Chem. Eng. Progress* **43**, 515 (1947).
[5] Robey, Wiese, and Morrell, *Ind. Eng. Chem.* **36**, 3 (1944).
[6] Roberts, Walton, and Morrell, *J. Research Natl. Bur. Standards* **38**, 627 (1947).
[7] McAdams, "Heat Transmission", 2nd Ed., New York, **1941**.
[8] Winding, Baumann and Kranich, *Chem. Eng. Progress* **43**, 527 (1947).
[9] Olsen, Brunjes, and Olsen, *Ind. Eng. Chem.* **22**, 1316 (1930).

TRANSPORT AND EQUILIBRIUM PHENOMENA IN GAS–ELASTOMER SYSTEMS.*

I. KINETIC PHENOMENA

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Recently attention has been directed to the more fundamental aspects of transport phenomena in elastomers. Permeability and diffusion constants for a large number of gas–elastomer and vapor–elastomer systems now available[1] were obtained by using the flow method as employed by Barrer[2] and by Daynes[3], and by studying sorption kinetics in the bulk material[4]. Interpretation of the process of diffusion in terms of the transition-state theory[5] and the statistical-kinetic theory[6] indicates that, for each unit act of the diffusion process to take place, a considerable zone of activation is necessary. An expression has been obtained, based on statistical considerations, for the size of a zone of activation in diffusion and in the related process of viscous flow[7].

Although attempts have been made to develop the statistical mechanics of cross-linked elastic networks, the parallel influence of cross-linking on transport processes has been little studied. The present paper is concerned with such nonequilibrium properties. Nitrogen, ethylene, and the normal paraffins from methane to butane were used so that the influence of molecular dimensions and chain length could be measured in permeation and diffusion where the elastomer, too, was systematically modified by more and more cross-linking. The data could then be used to examine the adequacy of the zone theory of diffusion in media in which the mesh of the network is continually decreased. In this connection it is already known that ebonite—nonelastic and representing the limit of the cross-linking process—shows a far greater molecular sieve activity in permeation and diffusion than does rubber[8].

EXPERIMENTAL

The apparatus employed for the determination of permeability and diffusion constants is illustrated diagrammatically in Figure 1. Two diffusion cells were used, one of a type already described[9], the other (Figure 2) built in two main sections. The membrane is placed in the lower half, supported from below by a fine copper gauze. The upper half is carefully placed on top of this system and screwed down by six screws. To complete the seal, mercury is poured into the annular space between the upper and lower sections. The copper leads from the cell are connected to the glass apparatus by means of vacuum wax, and to prevent any softening of the wax at higher temperatures, water is circulated through metal coils surrounding the junction of the copper and glass. Both diffusion cells are placed in copper vessels just large enough to contain them, packed with cotton wool to reduce convection, and im-

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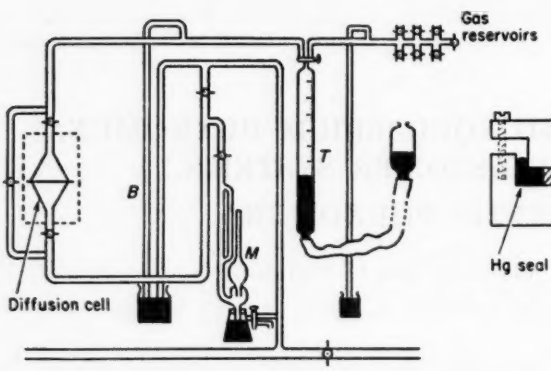

FIG. 1.—Layout of apparatus for determination of permeability and diffusion constants.

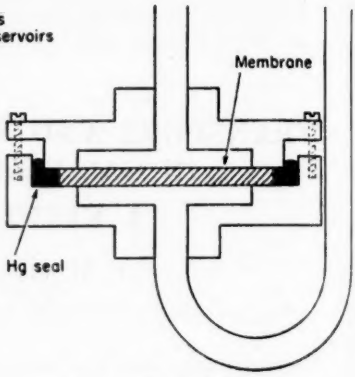

FIG. 2.—Permeability cell (second type).

mersed in a thermostat controlled to ±0.1° C. The low pressure side of each diffusion system is connected to a McLeod gage (*M*) capable of reading to 1.5 mm. with an accuracy of 0.005 mm. Hg.

Natural-rubber membranes[10] of known degree of vulcanization and approximately 1 mm. thick were provided by the British Rubber Producers' Research Association. A sample of Butyl rubber was provided by the Research Association of British Rubber Manufacturers, who supplied the foregoing information concerning its composition.

Constituents	Parts by weight
G.R.I. (Butyl rubber)[a]	100
Sulfur	2
Zinc oxide	5
Stearic acid	3
Tetramethylthiuram disulfide	1.0
Zinc diethyldithiocarbonate	1.5

[a] The stock was cured at 153° C for 30 minutes.

The following gases were employed.

Nitrogen.—Cylinder nitrogen was passed over a mixture of copper and copper oxide at 300–350° C (to remove hydrogen and oxygen), then through a tube of phosphoric oxide, and finally through a trap cooled in solid carbon dioxide. The gas was collected under vacuum conditions.

Methane.—Methane was prepared via the Grignard reagent of the type CH_3MgI made by the action of dry distilled methyl iodide and amyl ether on clean magnesium ribbon. Excess methyl iodide was distilled off and the magnesium methyl iodide decomposed in an evacuated system by the slow addition of water. The evolved methane was passed through a tube of phosphoric oxide and through a trap cooled in solid carbon dioxide, and collected in an evacuated reservoir.

Ethane and ethylene.—These gases were passed from cylinders over phosphoric oxide and a trap cooled at −78° C, and collected *in vacuo*. Analysis of the ethylene showed less than 2 per cent impurities.

Propane.—Propane, also taken from a cylinder, was passed over phosphoric oxide, collected in a trap at −78° C, and redistilled—the middle fraction being collected in a previously degassed reservoir.

n-Butane.—*n*-Butane was prepared in a manner similar to methane (via *n*-butyl magnesium iodide). After passing through a tube of phosphoric oxide it was condensed at −78° C and redistilled.

METHOD OF OPERATION

The whole diffusion cell is first thoroughly degassed at a fairly high temperature and the thermostat adjusted to the required temperature. By means of the Toepler pump (*T*), gas is introduced to the unsupported side of the membrane, the pressure being indicated by barometer (*B*). Throughout the experiment the pressure is kept constant by manipulation of the Toepler pump. The gas permeates through the membrane into a vacuum chamber of known volume, and the increase in pressure with time is followed by a McLeod gage, and a pressure *vs.* time plot is made (Figure 3). The experiment is continued

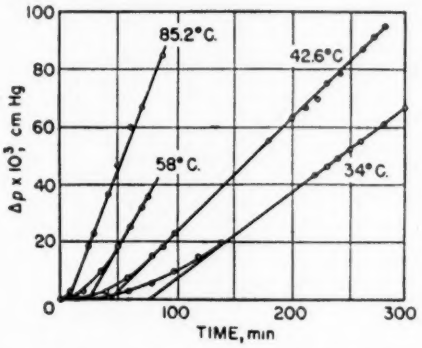

FIG. 3.—Rates of growth of pressure on the vacuum side of the membrane showing asymtotic approach to a steady state. Propane-natural rubber, 1.7 per cent combined S.

until the slope becomes constant when the steady state of flow has been established. From the steady state the permeability constant P may be calculated:

$$P = \frac{273}{T} \cdot \frac{V}{p_1} \cdot \frac{l}{a} \cdot \frac{\Delta p}{l} \cdot \frac{1}{76} \tag{1}$$

V = volume of the vacuum chamber; l = thickness of the membrane of area a; Δp = increase in pressure in time t; T = temperature of the vacuum chamber at room temperature, in degrees Kelvin; and p_1 is the pressure on the high-pressure side of the membrane.

If the intercept of the steady state of flow on the time axis is L, the diffusion constant[2] is given by:

$$D = l^2/6L \tag{2}$$

It may be shown[1] that it is safe to assume that the steady state has been reached after a time interval of approximately 2½ to 3 times the time lag L.

The inverse proportionality between the time lag and the diffusion constant make it difficult to measure certain diffusion constants when the time lag, if measured, would have been in the order of days.

RESULTS

Permeability and diffusion constants were measured at a number of different temperatures, and plots of $\log_{10} P$ and $\log_{10} D$ against $1/T$ (T in degrees Kelvin) made for each system (*e.g.*, Figures 4 and 5). From the smoothed curves the values in Table I were taken.

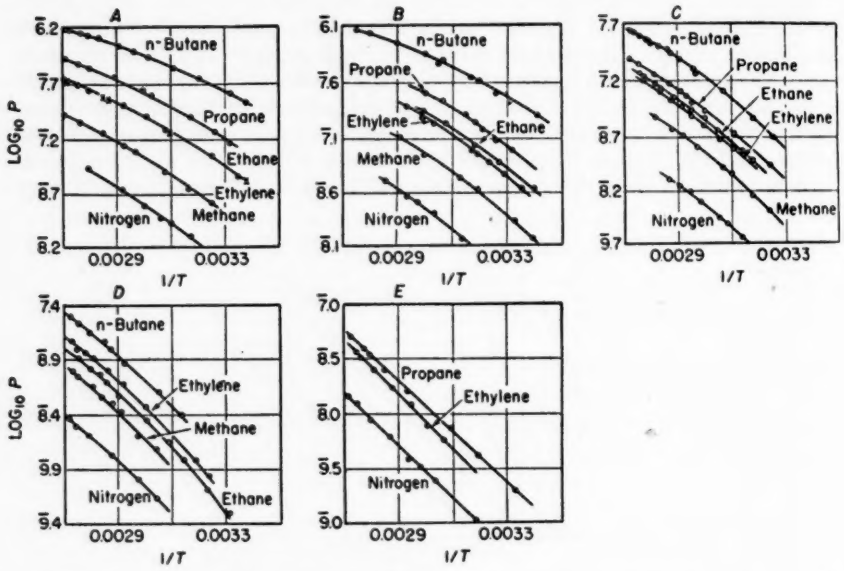

FIG. 4.—Curves of log P_{10} *vs.* $1/T$ showing gradual curvature in natural rubber and the absence of curvature in Butyl rubber: *A*, natural rubber with 1.7 per cent combined sulfur; *B*, natural rubber with 2.9 per cent combined sulfur; *C*, natural rubber with 7.15 per cent combined sulfur; *D*, natural rubber with 11.3 per cent combined sulfur; *E*, Butyl rubber.

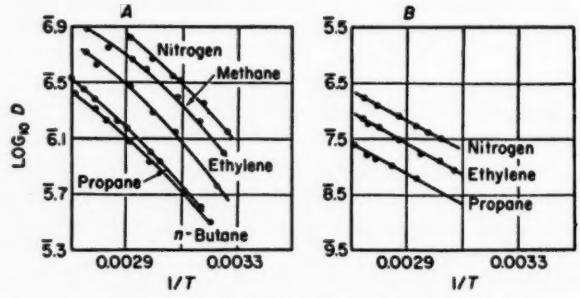

FIG. 5.—Plot of log D *vs.* $1/T$ showing gradual curvature in natural rubber with 1.7 per cent combined sulfur (*A*), and absence of curvature in Butyl rubber (*B*)

It is evident that as the percentage of the sulfur increases, the permeability and the diffusion constants decrease. This decrease is proportionately greater for the larger sized molecules and the tendency to molecular-sieve behavior is pronounced (Figures 6 and 7). In no case is the relationship between permeability or diffusion constants and the sulfur content a linear one. Although this is contrary to the findings of Carpenter and Twiss[4], and van Amerongen[9],

TABLE I

PERMEABILITY AND DIFFUSION CONSTANTS[a]

Membrane	Gas	Permeability constant			Diffusion constant, cm.² sec.⁻¹		
		40° C	60° C	80° C	40° C	60° C	80° C
Natural rubber, 1.7% S	Nitrogen	17.3×10^{-9}	38.9×10^{-9}	74.0×10^{-9}	199.0×10^{-8}	441×10^{-8}	851×10^{-8}
	Methane	50.1	109.0	186.0	145.0	345	640.0
	Ethane	126.0	250.0	399.0	54.0	150	308.0
	Ethylene	129.0	250.0	407.0	78.0	196	407.0
	Propane	224.0	417.0	630.0	34.0	92.5	200.0
	Butane	550.0	691.0	1230.0	34.0	81.4	178.0
Natural rubber, 2.9% S	Nitrogen	12.6×10^{-9}	28.0×10^{-9}	57.5×10^{-9}	157×10^{-8}	360×10^{-8}	720×10^{-8}
	Methane	41.3	93.3	170.0	104.0	255.0	497.0
	Ethane	107.0	224.0	390.0	47.7	121.0	255.0
	Ethylene	73.3	199.0	363.3	83.0	168.0	335.0
	Propane	168.0	323.0	518.0	32.6	932.0	201.0
	Butane	412.0	724.0	1080.0	23.0	670.0	156.0
Natural rubber, 7.15% S	Nitrogen	4.07×10^{-9}	11.7×10^{-9}	24.5×10^{-9}	52.5×10^{-8}	151×10^{-8}	316×10^{-8}
	Methane	12.9	34.2	72.4	33.4	103.0	244
	Ethane	24.5	63.0	12.9	12.3	39.8	101
	Ethylene	27.0	64.0	141.3	10.7	58.1	140
	Propane	34.0	81.3	166.0	5.92	19.6	54.0
	Butane	66.0	166.0	330.0	2.96	13.5	42.5
Natural rubber, 11.3% S	Nitrogen	1.66×10^{-9}	5.6×10^{-9}	13.6×10^{-9}	23.2×10^{-8}	79.0×10^{-8}	19.1×10^{-8}
	Methane	3.6	15.5	39.8	—	53.3	148
	Ethane	6.9	23.0	60.2	3.6	16.3	52.5
	Ethylene	9.3	29.5	70.8	6.10	23.6	66.6
	Propane	5.75	25.7	63.6	1.15	6.8	23.8
	Butane	17.0	53.7	122.0	1.025	5.38	19.8
Natural rubber, 15.15% S	Methane	1.13×10^{-9}	5.01×10^{-9}	15.1×10^{-9}	—	18.4×10^{-8}	65.9×10^{-8}
Natural rubber, 21.9% S	Nitrogen	—	0.23×10^{-9}	0.85×10^{-9}	—	6.53×10^{-8}	23.4×10^{-8}
	Methane	—	—	1.26	—	—	8.4
Butyl rubber	Nitrogen	0.95×10^{-9}	2.88×10^{-9}	7.4×10^{-9}	13.5×10^{-8}	40.3×10^{-8}	107×10^{-8}
	Ethylene	2.8	8.6	23.0	4.07	14.0	40.5
	Propane	3.98	11.2	28.0	1.23	4.07	11.7

[a] Permeability constants are given throughout as cubic centimeters of gas at N.T.P. passing through 1 sq. cm. of a membrane 1 mm. thick when the pressure difference across the membrane is 1 cm. of Hg.

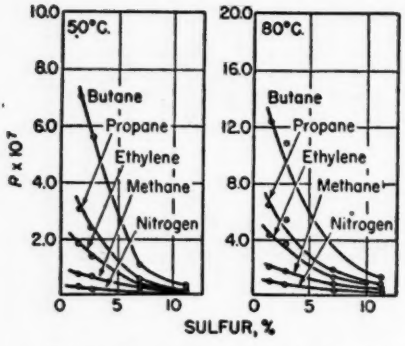

FIG. 6.—Permeability constants as a function of the percentage of combined sulfur in natural vulcanizates.

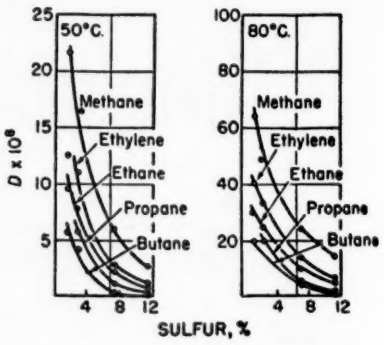

FIG. 7.—Diffusion coefficients as a function of the percentage of combined sulfur in natural vulcanizates.

these authors covered only the range of sulfur contents <5 per cent S for the diffusion of nitrogen, and any departure from linearity could then easily have been missed.

The effect of molecular dimensions upon permeability and diffusion constants is shown in Figures 8 and 9 in which P and D are plotted against the number of carbon atoms in the hydrocarbon molecule. It is seen that, whereas in any one membrane the diffusion constant increases in the expected manner from butane to methane, the permeability constant decreases. This is due to the composite nature of P[11]. A decrease in D in passing from methane to butane is more than offset by an increase in the solubility constant (see Part II).

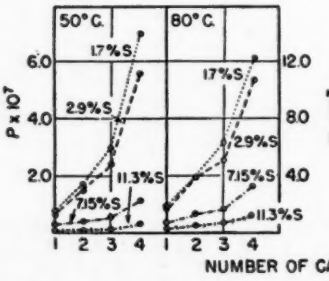

FIG. 8.—Dependence of permeability constant on the number of carbon atoms in simple n-paraffins.

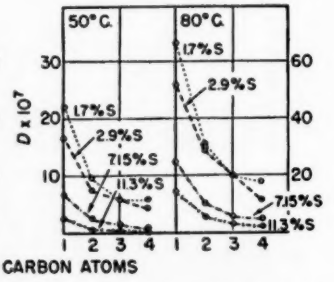

FIG. 9.—Dependence of diffusion coefficient on the number of carbon atoms in simple n-paraffins.

TEMPERATURE COEFFICENTS OF PERMEATION AND DIFFUSION

Hitherto the relationship between $\log_{10} P$ and $1/T$ has been found to be linear[12], *i.e.*, the equation:

$$P = P_0 e^{-E_P/RT} \tag{3}$$

has been found to hold where P_0 is a constant and E_P is the apparent energy of activation for permeation—also constant. Over an extended temperature range, however, we have consistently observed curvature in graphs of $\log_{10} P$ *vs.* $1/T$ for all the natural rubber vulcanizates (Figures 4 and 5). In interesting contrast to this, no departure from linearity was observed in the case of Butyl

rubber (Figure 4). Recalling the composite nature of P, curvature of plots of log P *vs.* $1/T$ is to be traced back to curvature in the plots of $\log_{10} D$ *vs.* $1/T$ (Figure 5) as ΔH (the heat of solution) remained constant over a range of temperatures (see Part II).

TABLE II

APPARENT ENERGIES OF ACTIVATION FOR PERMEATION AND DIFFUSION AT 60° C

Membrane	Gas	E_P (cal./mole)	E_D (cal./mole)
Natural rubber (1.7% S)	Nitrogen	7,900	8,000
	Methane	7,250	8,250
	Ethane	6,500	8,850
	Ethylene	6,500	8,900
	Propane	5,750	9,750
	Butane	4,200	8,900
Natural rubber (2.9% S)	Nitrogen	8,500	8,500
	Methane	7,700	8,520
	Ethane	6,900	9,000
	Ethylene	6,800	9,300
	Propane	5,600	9,000
	Butane	5,300	10,800
Natural rubber (7.15% S)	Nitrogen	9,900	9,700
	Methane	9,200	10,600
	Ethane	8,450	10,700
	Ethylene	8,600	10,600
	Propane	8,100	11,500
	Butane	8,000	13,700
Natural rubber (11.3% S)	Nitrogen	11,000	11,000
	Methane	11,000	12,300
	Ethane	11,000	13,100
	Ethylene	10,600	12,600
	Propane	12,000	15,400
	Butane	10,600	15,800
Natural rubber (15.15% S)	Methane	≈13,800	≈14,300
Butyl rubber	Nitrogen	11,300	11,300
	Ethylene	11,400	12,300
	Propane	10,700	12,600

Values of E_D, the apparent energy of activation for diffusion, and of E_P, the apparent energy of activation for permeation, calculated for 60° C, are given in Table II. From this table one sees to what extent molecular size or mass modifies the magnitude of E_P for degrees of vulcanization up to 11.3 per cent sulfur. In this range the order:

$$E_D \text{ butane} > E_D \text{ propane} > E_D \begin{matrix}\text{ethane}\\\text{ethylene}\end{matrix} > E_D \text{ methane} > E_D \text{ nitrogen}$$

tends to be preserved. As the degree of vulcanization increases, some increase in E_P is evident, this increase being greatest for the largest molecules. The explanation of the above behavior again lies in the composite nature of $E_P (E_P = E_D + \Delta H)$. The last column of Table II shows that E_D increases as the molecular size increases, but on the other hand this is offset by a corresponding increasingly negative heat of solution, ΔH. As the degree of cross-linking becomes high, however, E_D increases more rapidly for large than for small molecules than does the negative value of ΔH (see Part II). It is also seen that the sequence of values of E_D is:

$$E_D \text{ butane} > E_D \text{ propane} > E_D \begin{matrix}\text{ethane}\\\text{ethylene}\end{matrix} > E_D \text{ methane} > E_D \text{ nitrogen}$$

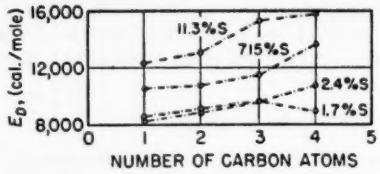

FIG. 10.—Dependence of energy of activation for diffusion in natural rubber vulcanizates on the number of carbon atoms in simple *n*-paraffins.

The increase of E_D with chain length in various vulcanizates is shown in Figure 10.

The extent to which E_P depends on temperature is shown in Table III, which also contains values of E_P for the systems, CH_4 and N_2–21.9 per cent sulfur vulcanizate, and CH_4–15.15 per cent sulfur vulcanizate, at 80° C, which could not be measured accurately below 60° C.

TABLE III

VARIATION OF E_P WITH TEMPERATURE

Membrane	Gas	80° C	50° C	30° C
1.7% S	Butane	3,800	5,000	5,950
11.3% S	Ethylene	9,400	12,300	—
15.15% S	Methane	11,500	—	—
21.9% S	Nitrogen	15,000	—	—
21.9% S	Methane	20,000	—	—

Van Amerongen[9] has recently suggested that there may be a relationship between the cohesive energy of an elastomer and the energy of activation for diffusion of a gas in the elastomer. This suggestion is supported by data for diffusion through butadiene polymer, and methyl and natural rubbers. While there may be some relationship between cohesive density and E_D, this alone cannot fully explain our results. There is evidence that the cohesive energy density of natural rubber is not appreciably altered as the degree of vulcanization is increased[13], and if this were the only factor controlling E_D, the energy of activation would be constant for various sulfur contents. The increase in E_D with increasing sulfur content is evident from Table II.

ORIGIN OF E_D

E_D is the energy required for completion of 1 Avogadro number of unit diffusion processes. Presumably it involves the work of separation of chains, and, in the absence of specific interactions between the groups of the elastomer and the diffusing particle, some increase in E_D with molecular size might be expected. According to the zone theory[7], transport takes place when local conditions are favorable, *i.e.*, when the concentration of thermal energy is sufficient to enable an adequate localized chain separation and loosening to take place. An increase in E_D means either an increase in the energy required per unit chain separation or else an increase in the zone size if the energy required per unit chain separation is constant. Now the heat of solution in the elastomer and consequently its cohesive energy density does not alter over a range in the degree of vulcanization (see Part II). Thus the energy required for loosening a chain segment is probably constant, and, therefore, the zone

size must increase as the degree of vulcanization and the molecular size of the diffusing particle increase. The number of chain segments to be loosened for a successful unit diffusion process for a nitrogen molecule is smaller and should involve fewer of the permanent cross-linkages than would the transport of a large molecule such as butane. For butane, not only should the zone of activation be larger in the absence of cross-linking, but in a vulcanizate, further segments, unaffected in the absence of the cross-links, should become displaced. Thus a small molecule may require for transport the loosening of not many more chain segments in a moderately vulcanized elastomer than in a lightly vulcanized stock, whereas, for the larger molecules, the number of segments to be loosened may be proportionately greater in the moderately vulcanized stock. The larger zone size is manifest in a larger D_0 value, where D_0 occurs in the expression:

$$D = De^{-E_0/RT} \tag{3a}$$

Table IV lists values of D_0 calculated from the slopes of $\log_{10} D$ *vs.* $1/T°$ K plots at 60° C. The expected increase in D_0 with increasing degree of vulcanization particularly with larger sized molecules is quite clear.

TABLE IV

D_0 VALUES AT 60° C FOR DIFFUSION THROUGH NATURAL RUBBER

D_0	Nitrogen	Methane	Ethane	Ethylene	Propane	Butane
1.7	0.74	0.83	0.86	1.23	2.1	0.53
2.9	1.26	0.925	0.91	1.9	1.8	7.43
7.15	3.24	8.3	3.84	4.5	6.2	120.0
11.3	12.0	57.0	58.0	39	680	1175.0

INTERPRETATION OF D_0

According to the transition state theory[14].—The expression for D_0 given by the transition state theory is:

$$D_0 = e^{\Delta S‡/R} \cdot \frac{kT}{h} \cdot d^2 \cdot \frac{1}{2.72} \tag{4}$$

$$\Delta S‡ = R\left[\ln D_0 - \ln \frac{kT}{2.72}\frac{d^2}{h}\right] \tag{5}$$

$\Delta S‡$ is the entropy of activation; k and h are, respectively, the Boltzmann and Planck constants; and d is the mean distance moved by the solute in a unit diffusion process.

Values of $\Delta S‡$ and the corresponding $\Delta G‡$ values are tabulated in Table V assuming a value for d^2 of 10^{-15} cm.^{2}.

According to the zone theory[7].—The complete expression for D is:

$$D = \nu d^2 \cdot e^{-E/RT} \cdot \sum_{f=1}^{n} \left(\frac{E_1}{RT}\right)^{f-1} \cdot \frac{1}{(f-1)!}\rho_f \tag{6}$$

where f is the number of degrees of freedom among which the total activation energy E_1 is shared in any zone, the summation being taken up to n; n is the number of degrees of freedom in the largest, *i.e.*, most diffuse, zone of activation contributing appreciably to D; ν is the mean vibration frequency of the diffusing molecule relative to its environment; and d the mean distance moved in a unit

diffusion process. The factor ρ_f is introduced to allow for the possible need for synchronized movements of the diffusing molecule and of neighboring polymer segments to consummate a unit diffusion process. When Schottky defects or holes move in a cubic lattice, for instance, ρ_f is 1/6. For place exchange diffusions, however, ρ_f has the form $\sum(1/m)^p$ if one out of m preferred directions must be taken by each of p particles. The summation is required because for any one zone of activation a number of such sets of synchronized motions may bring about a unit diffusion process[15].

TABLE V

$\Delta S\ddagger$ AND $\Delta G\ddagger$ VALUES AT 60° C

Combined sulfur in rubber (%)	Nitrogen	Methane	Ethane	Ethylene	Propane	Butane
			$\Delta S\ddagger$ in e.u. (entropy units)			
1.7	11.4	11.6	11.6	12.4	13.4	10.5
2.9	12.4	11.8	11.7	13.2	13.0	15.9
7.15	14.4	16.2	14.7	14.9	15.6	21.5
11.3	16.9	20.0	20.0	19.3	25.0	26.0
			$\Delta G\ddagger$ in cal./mole			
1.7	3500	3700	4400	4150	4700	4750
2.9	3750	4000	4450	4200	4700	4900
7.15	4300	4000	5200	4950	5600	5900
11.3	4750	5050	5850	5500	6400	6500

To determine f, Equation (6) must be simplified. One term is assumed to be dominant and is used alone to give D. If, in addition, f for the dominant term is independent of temperature, one finds on equating the simplified version of equation (6) to the Arrhenius equation, $D = D_0 e^{-E_D/RT}$, and using Stirling's approximation for the factorial, that:

$$E_1 = E_D + (f - 1)RT \tag{7}$$

and:

$$\log_{10} D_0 = \log_{10} (\rho_f \cdot \nu d^2) + (f - 1) \log_{10} \left(\frac{E_D + (f - 1)RT}{RT} \right) - (f - 1) \log_{10} (f - 1) - \tfrac{1}{2} \log_{10} 2\pi(f - 1) \tag{8}$$

By first plotting the right hand side of Equation (8) against f for different values of f, one may then read off from the curve the value of f required to give any experimental value of log D_0 (Figure 11). Values of f thus obtained taking the value of $\rho_f = 1/6$, $\nu = 2.5 \times 10^{12}$ sec.$^{-1}$, and $d^2 = 10^{-15}$ cm.^{2}, are given in Table VI.

f so calculated is sensitive to the value of the product $\rho_f \nu d^2$, as is stressed by Table VII and Figure 11, which indicate the results of taking $\rho_f = 1/6$, coupled with:

$d^2 = 10^{-15}$ cm.^{2}	$\nu = 2.5 \times 10^{12}$ sec.$^{-1}$	(curve *a*)
$d^2 = 2.5 \times 10^{-15}$ cm.^{2}	$\nu = 2.5 \times 10^{12}$ sec.$^{-1}$	(curve *b*)[2]
$d^2 = 6.4 \times 10^{-15}$ cm.^{2}	$\nu = 5 \times 10^{12}$ sec.$^{-1}$	(curve *c*)[1]

TABLE VI

NUMBER OF DEGREES OF FREEDOM (f) SHARING IN THE DIFFUSION PROCESS

Sulfur (%)	Gas	80° C	60° C	50° C
1.7	Methane	16	24	26
1.7	Ethylene	15	21	22
1.7	Propane	17	20	21
1.7	Butane	14	15	17
2.9	Methane	19	24	24
7.15	Ethane	20	21	20
11.3	Butane	26	28	—
1.7	Nitrogen	—	27	—
2.9	Nitrogen	—	28	—
7.15	Nitrogen	—	25	—
11.3	Nitrogen	—	28	—
Butyl rubber	Nitrogen	—	21	—
	Ethylene	—	20	—
	Propane	—	15	—

TABLE VII

Gas	Combined sulfur in rubber (%)	D_0, cm.² sec.⁻¹	f at 60° C: From curve (a) Fig. 11	From curve (b) Fig. 11	From curve (c) Fig. 11
Methane	2.9	0.925	24	15	7
Ethylene	1.7	1.23	21	14	7
Porpane	7.15	6.2	19	14	9
Butane	11.3	1175	28	19	11

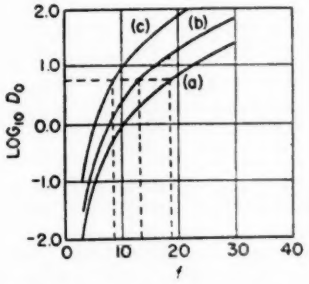

FIG. 11.—$\text{Log}_{10} D_0$ plotted against f, used to determine possible values of f for propane diffusing in rubber with 7.15 per cent sulfur S. P_f for curves a, b, c is taken to be 1/6. Curve a: $\nu = 2.5 \times 10^{12}$ sec.⁻¹, $d^2 = 10^{-15}$ cm.². Curve b: $\nu = 2.5 \times 10^{12}$ sec.⁻¹, $d^2 = 2.5 \times 10^{-15}$ cm.². Curve c: $\nu = 5 \times 10^{12}$ sec.⁻¹, $d^2 = 6.4 \times 10^{-15}$ cm.².

An interpretation of the analogous problem of viscous flow [15] suggested values of ρ_f of 1/6 to about 10^{-3}, so the range in $\rho_f \nu d^2$ may be appreciable.

A second approach to the value of f follows from Equation 7, which shows that $dE_D/dT = -(f-1)R$, provided that f is independent of T. Typical values of f thus calculated for a membrane containing 1.7 per cent combined sulfur are:

Gas	Temperature range (° C)	f
CH_4	30–50	30
CH_4	50–80	41
C_2H_4	30–90	35
C_3H_8	50–80	31

Thus, while there is uncertainty as to the precise value of f there seems no doubt that an appreciable zone of activation is necessary for a unit diffusion process to take place. This view is further supported by the magnitude of the energies and entropies of activation for diffusion and flow in elastomers, compared with monomeric liquids, even where cohesive energy densities of polymer and liquid are similar.

FUNCTIONAL RELATIONSHIPS

Linear relationships have been observed when $\Delta S\ddagger$ or $\log_{10} D_0$ is plotted against E_D for a number of diffusion systems[16]. Barrer[15] has shown, however, that the most general relationship is between $\log_{10} D_0$ and E_D/T. Accordingly earlier data[12] are combined in Figure 12 with those obtained in the present work. The corresponding relation between $\Delta S\ddagger$ and E_D/T becomes:

$$\Delta S\ddagger = -4.6 + 0.65(E_D/T) \tag{9}$$

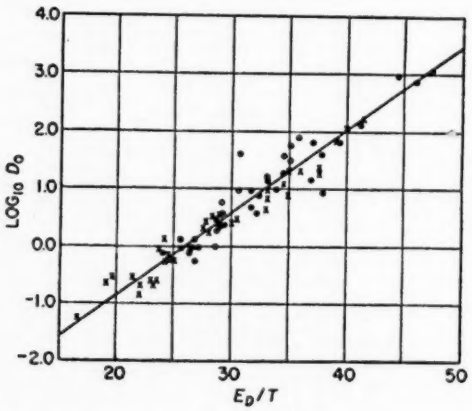

FIG. 12.—Functional relation between $\log_{10} D_0$ and E_D/T for diffusion in numerous elastomers: (●) authors; (○) footnote 4; (×) footnote 1.

One may consider and seek to differentiate between two alternative interpretations of such relationships. For a given type of medium (*e.g.*, molecular liquids) the larger E_D/T, the larger is the zone of activation. If the zone size is further assumed to be directly proportional to E_D/T, it has already been shown that the functional relationship between $\log_{10} D_0$ and E_D/T results[15].

However, a second possibility arises. In the Arrhenius equation $D = D_0 e^{-E_D/RT}$ (and similarly for any other activated rate process) the range in $\log_{10} D$ is considerably smaller than that in $E_D/4.60T$. To a first approximation, then, take $\log_{10} D$ to be constant. One now has:

$$\log_{10} D_0 = \log_{10} D + E_D/4.60T \simeq \text{constant} + 0.217\, E_D/T \tag{10}$$

The slope 0.217 of the curve of $\log_{10} D_0$ vs. E_D/T should be a universal one for this and all rate processes. For systems examined, one finds:

(i) $\log_{10} D_0 = -3.6 + 0.14\ E_D/T$ (this paper)
(ii) $\log_{10} \phi_0 = 2.43 + 0.16_7\ E_\phi/T$ (for fluidity, ϕ)[15]
(iii) $\log_{10} \phi_0 = 0 + 0.11_5\ E_\phi/T$ (for fluidity, ϕ)[15]
(iv) $\log_{10} k_0 = -4.6_6 + 0.23_5\ E_r/T$ (for reactions of first order)

where (ii) and (iii) refer to viscous flow of molecular liquids and of polymerized ionic melts, respectively; and (iv) refers to a group of 42 first-order homogeneous gas reactions. The slopes for the physical rate processes are all very similar and less than 0.217, as required by Equation (10). However, it is not correct to take $\log_{10} D$ or $\log_{10} \phi$ as strictly constant—the variation in $\log_{10} \phi$, for example, is up to 25 per cent of the variation in $E_\phi/4.60T$, large values of ϕ being associated with small values of $E_\phi/4.60T$; and this will tend to make the apparent slopes of the mean straight lines (i) to (iii) rather less than 0.217.

Thus the evidence, although not wholly conclusive, seems to make the interpretation of the observed functional relationships given in the preceding paragraph a very natural one.

SUMMARY

The influence has been studied of systematic alterations in the extent of cross-linking in elastomers on diffusion coefficients and permeability constants in elastomers of homologous paraffin hydrocarbons. In a number of such media the influence of chain length of the paraffins on the transport phenomena has also been investigated, using CH_4, C_2H_6, C_2H_4, C_3H_8, and n-C_4H_{10}.

Apparent activation energies for permeation (E_P) and for diffusion (E_D) for degrees of vulcanization up to 11.3 per cent combined sulfur are in the decreasing order:

$$\text{butane} > \text{propane} > \begin{matrix}\text{ethane} \\ \text{ethylene}\end{matrix} > \text{methane} > \text{nitrogen}$$

For low vulcanizates, E_P is not very sensitive to the percentage of sulfur. However for higher percentages of sulfur, E_P tends to rise, especially when the migrating molecule is a large one. E_D is rather more sensitive both to molecular size and to percentage of combined sulfur.

Both E_P and E_D for natural rubber vulcanizates show definite temperature coefficients, manifested as curvature when $\log_{10} D$ or $\log_{10} P$ is plotted against $1/T$. Such curvature was absent, however, in Butyl rubber.

The results have been interpreted in terms of the molecular nature of elastic networks and in terms of the kinetic-statistical (zone) theory and the transition-state theory. All treatments indicate the need for a considerable zone of activation for each unit diffusion process, confirming an earlier investigation. When, in the Arrhenius equation, $D = D_0 e^{-E_D/RT}$, one plots $\log_{10} D_0$ against E_D/T, the clear functional relationship:

$$\log_{10} D_0 = -3.6 + 0.14\, E_D/T$$

emerges. A simple interpretation of this and of similar functional relationships for other activated physical and chemical rate processes has been given.

ACKNOWLEDGMENT

One of us (G. Skirrow) is glad to acknowledge the award of a Junior Harlow Fellowship, which made his participation in the work possible.

REFERENCES

[1] Van Amerongen, *Rev. gén. caoutchouc* **12**, 99 (1940); *J. Applied Physics* **17**, 972 (1946); Doty, Aikens, and Mark, *Ind. Eng. Chem.* **36**, 686 (1944); Doty, *J. Chem. Physics* **14**, 244 (1945).
[2] Barrer, *Trans. Faraday Soc.* **35**, 628, 644, 645 (1939); **36**, 344 (1940).
[3] Daynes, *Proc. Roy. Soc. London* **A97**, 286 (1920).
[4] Carpenter and Twiss, *Ind. Eng. Chem. Anal. Ed.* **12**, 99 (1940).
[5] Eyring, *J. Chem. Physics* **4**, 283 (1936).

[6] Carpenter and Twiss, *Ind. Eng. Chem. Anal. Ed.* 12, 99 (1940); Glasstone, Laidler and Eyring, "Theory of Rate Processes", New York, 1941; Barrer, *Trans. Faraday Soc.* 38, 322 (1942).
[7] Barrer, *Trans. Faraday Soc.* 38, 322 (1942).
[8] Barrer, *Trans. Faraday Soc.* 36, 644 (1940).
[9] Van Amerongen, *J. Applied Physics* 17, 972 (1946).
[10] The membranes were prepared from smoked sheet rubber and milled to a molecular weight of about 100,000. Curing was carried out under steam pressure, and the membranes were extracted with acetone. The ash was of the order of 1–2 per cent, after the previous analysis. No fillers were present.
[11] P is proportional to both diffusion and solubility constants.
[12] Barrer, *Trans. Faraday Soc.* 35, 628, 644, 645 (1939); 36, 644 (1940); Van Amerongen, *Rev. gén. caoutchouc* 12, 99 (1940); *J. Applied Physics* 17, 972 (1946).
[13] This seems a reasonable assumption in view of the constancy of the heat of solution, given in Part II, through the range of sulfur contents studied, and of the relationship between heat of solution and C.E.D. (*cf.* Hildebrand, "Solubility", New York, 1936).
[14] Glasstone, Laidler and Eyring, "Theory of Rate Processes", New York, 1941.
[15] Barrer, *Trans. Faraday Soc.* 39, 48, 59 (1943).
[16] Barrer, *Trans. Faraday Soc.* 38, 322 (1942); Doty, *J. Chem. Physics* 14, 244 (1945); Van Amerongen, *Rev. gén. caoutchouc* 12, 99 (1940); *J. Applied Physics* 17, 972 (1946). P is proportional to both diffusion and solubility constants.

II. EQUILIBRIUM PHENOMENA

INTRODUCTION

The solubility of gases in liquids and elastomers is attracting increasing attention. Some aspects of this problem for monomeric solvents have been considered by Horiuti[1] and others[2], and theoretical treatments of particular solvents such as water have been given by Eley[3]. A special topic is the behavior of polymer–monomer mixtures, where the large entropy of mixing has been explained on a statistical mechanical basis[4]. Included in such systems are gas–elastomer mixtures, which have been the subject of several investigations. The solubility constant of a gas above its critical temperature in an elastomer can be calculated with some accuracy by equating the partition function for the gas in the gas phase to the partition function for the dissolved gas with which it is in equilibrium[5]. A configurational term arises in the partition function of the dissolved gas just as it arises for monomeric liquids in elastomers[4], while the dissolved gas molecule otherwise behaves as a three-dimensional oscillator. A further semiempirical treatment of gas–elastomer equilibria is given by Gee[6].

Many solubility data in polymers suffer from the point of view of quantitative treatment because they refer to systems of industrial importance, such as filled, reinforced, plasticized stocks of unknown degree of vulcanization. Measurements more suitable for interpretation have been made by Barrer[7] and van Amerongen[8], using a dynamic method, and by Carpenter and Twiss[9], using a static method. Following these investigations we shall, in the present paper, investigate and attempt to interpret the effects of the degree of vulcanization of natural rubber on the solubility constants and related quantities for a series of simple homologous *n*-paraffins (methane to *n*-pentane).

EXPERIMENTAL

The materials employed were those of Part I of this paper[10]. Solubility constants were measured by two methods.

Dynamic method.—Having determined the permeability and diffusion constants[10], the solubility constant[11] σ may be calculated from the relationship: $P = D\sigma$.

Static method.—The apparatus illustrated diagrammatically in Figure 1 consists of a bulb B (in which is placed the elastomer—(0.5 gram) connected to a calibrated gas pipet P by a constriction C and a tap T_1. Tap T_2 of the gas

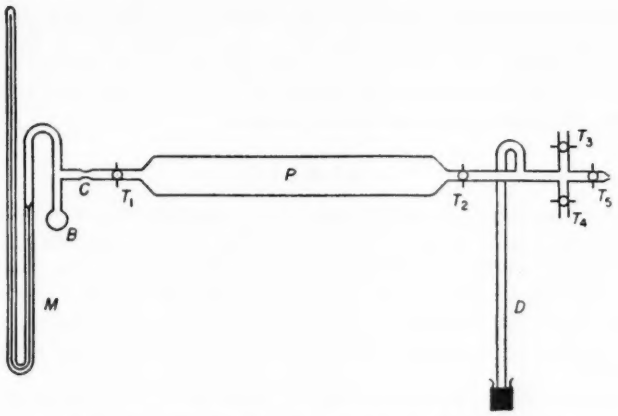

FIG. 1.—Apparatus for static method of determining solubilities.

pipet is connected to barometer D, a source of gas supply through T_3, and a vacuum pump system through T_4. The whole apparatus is first degassed, and the manometer M attached to D reads zero pressure. (T_3 and T_5 are closed.) T_1 and T_4 are then closed, and air is admitted to the pipet through tap and jet T_5 until a suitable pressure reading is obtained on D when T_5 and T_2 are closed. The calibrated pipet now contains air at a known pressure, and on opening T_1 the air expands into B and a pressure reading is obtained on M. This is repeated several times so that the volume (V_1) of B may be calculated. The whole apparatus is once more thoroughly degassed until the last traces of air are removed from the rubber, and butane is admitted to P through T_3 until a suitable reading is obtained on D when T_2 is closed. T_1 is opened and, as soon as the butane expands into B, the pressure on M is noted, and the constriction C is sealed with the tip of a blowpipe flame. The volume (x) of the end section between D and T_1 is determined by filling with mercury and weighing the mercury. The new volume (V_2) of the bulb is thus $V_1 - x$. As gas

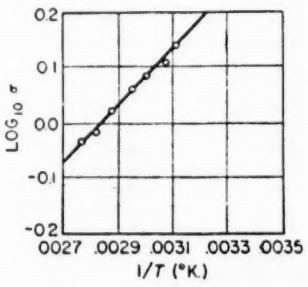

FIG. 2.—Solubility of ethane in natural rubber (7.15 per cent sulfur).

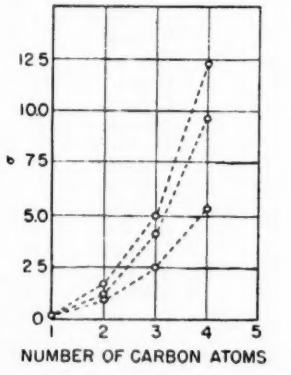

FIG. 3.—Influence of chain length on solubility of normal paraffins in a rubber vulcanizate (1.7 per cent sulfur).

dissolves in the rubber, the pressure indicated by M decreases and, from the equilibrium pressure, the initial pressure, the volume of the bulb, and the volume of the rubber, the solubility of the gas may be calculated. The bulb is immersed in a thermostat regulated to 0.1° C. The method was employed only for the solubility of butane and pentane.

RESULTS

Solubility constants for each system were calculated at a number of different temperatures, and plots of $\log_{10} \sigma$ against $1/T$ were made (Figure 2). From these plots the smooth values indicated in Table I were read off. The results for specimens containing 1.7 to 11.3 per cent sulfur are accurate to about 4 per cent; the results for higher degrees of vulcanization are less accurate, owing to the increased difficulty of measuring permeability and diffusion constants.

Variations and irregularities from sample to sample and deviations in results obtained with the dynamic and static methods are considered to be due primarily to irregularities in the structure of the rubber (*e.g.*, flaws).

TABLE I

SOLUBILITY OF GASES IN NATURAL AND BUTYL RUBBER

Sulfur (%)	Gas	Solubility		
		At 40° C	At 60° C	At 80° C
		NATURAL RUBBER		
1.7	Nitrogen	0.066	0.066	0.066
	Methane	0.262	0.238	0.22
	Ethane	1.6	1.23	0.98
	Ethylene	1.26	0.96	0.76
	Propane	5.01	3.38	2.4
	Butane	12.3	7.76	5.25
2.9	Nitrogen	0.061	0.061	0.061
	Methane	0.305	0.28	0.26
	Ethane	1.7	1.4	1.16
	Ethylene	1.05	0.9	0.785
	Propane	3.88	2.63	1.9
	Butane	13.3	8.2	5.25
7.15	Nitrogen	0.059	0.059	0.059
	Methane	0.294	0.255	0.226
	Ethane	1.51	1.2	0.975
	Ethylene	1.08	0.895	0.758
	Propane	4.36	3.16	2.34
	Butane	17.0	9.55	5.89
11.3	Nitrogen	0.054	0.054	0.054
	Methane	—	0.23	0.203
	Ethane	1.35	1.07	0.878
	Ethylene	1.16	0.953	0.804
	Propane	3.80	2.88	2.10
	Butane	12.6	7.59	4.78
15.5	Methane	—	0.204	0.178
21.9	Nitrogen	—	0.028	0.028
	Methane	—	0.10	0.10
		BUTYL RUBBER		
	Nitrogen	0.052	0.052	0.052
	Ethylene	—	0.484	0.42
	Propane	—	2.07	1.8

It is evident that up to 11.3 per cent sulfur the effect of vulcanization on solubility is much less than upon the diffusion constant[10]. This can arise because the volume-fraction of dissolved gas is too small to cause any appreciable extension of the rubber network and hence no effect of increased cross-linking is felt. Table II, which lists values of the solubility of butane and pentane

TABLE II

SOLUBILITY OF *n*-BUTANE AND *n*-PENTANE IN VULCANIZED NATURAL RUBBER
(Static method)

Sulfur (%)	Solubility							
	n-Butane				*n*-Pentane			
	80° C	60° C	50° C	40° C	80° C	60° C	50° C	40° C
1.7	5.6	8.3	10.5	13.2	11.2	20.4	28.1	38.0
2.9	5.7	9.1	12.2	15.05	8.7	15.5	21.0	30.2
7.15	3.6	5.75	7.6	10.23	7.4	12.3	16.5	22.5
11.3	3.89	6.09	7.94	10.47	—	—	—	—
15.5	—	—	—	—	6.4	11.0	14.5	20.0

in rubber obtained by the static method, indicates that there is a definite decrease in the solubility of pentane as the degree of cross-linking increases. This may be due to the larger volume fraction of the pentane, which has brought distension of the rubber networks to a point where cross-linking has started to impose restraints on swelling in the case of the more highly cross-linked vulcanizates. The effect on σ of increasing the number of carbon atoms in the hydrocarbon molecule is indicated in Figure 3.

Van Amerongen[8] has recently suggested that there is a linear relationship between $\log_{10} \sigma$ (at constant temperature for a given membrane) and the critical temperature of the gas. The suggestion is supported by Figure 4.

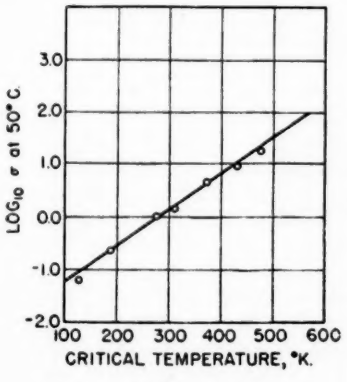

FIG. 4.—Solubility as a function of critical temperature (natural rubber 1.7 per cent sulfur).

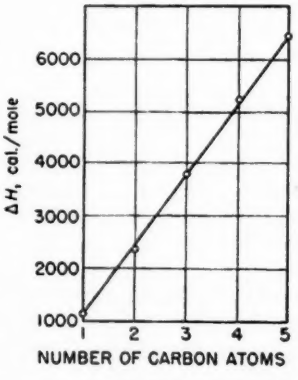

FIG. 5.—Relation between ΔH and chain length for normal paraffins.

The values of $\log_{10} \sigma$ are for the gases–nitrogen, methane, ethane, ethylene, propane, *n*-butane, and *n*-pentane, in a sample of natural rubber at 50° C. If there is a linear relationship of the type:

$$\log_{10} \sigma = a + bT_c \qquad (1)$$

then, once the constants a and b are determined for a given elastomer, it should be possible to predict the solubility of a gas merely from a knowledge of its critical temperature. It follows that the heat of solution should also be predictable.

From Figure 5, $\log_{10}\sigma = -2.0 + 0.007T_c$. Gee[6] has suggested the relationship:

$$-2.303\log_{10}\sigma = 4.5 + \mu - 10(T_b/T)$$

where μ is a constant and T_b is the boiling temperature. This may be adjusted by setting $T = 50°$ C, $T_b = T_c \times 0.6$ (Guldberg-Guye rule), and taking $\mu = 1.5$ (footnote 12). This gives:

$$\log_{10}\sigma = -2.6 + 0.008T_c$$

so that the two relationships are substantially equilvalent. Since Gee'se relation has some theoretical significance, the equivalence may be offered as a partial explanation of the relation between σ and T_c.

HEAT OF SOLUTION

The solubility constant σ thus far employed is identical with the Bunsen solubility coefficient, but an alternative solubility constant ρ may be identified with the Ostwald solubility coefficient:

$$\rho = \sigma(T/273)$$

For the Bunsen coefficient, $\sigma = \sigma_0 e^{-\Delta H/RT}$, and for the Ostwald coefficient, $\rho = \rho_0 e^{-\Delta U/RT}$, where $\Delta U = \Delta H + RT$.

Heats of solution calculated previously by Barrer[7] are ΔH values, while the values given by van Amerongen[8] are ΔU values[12]. Values of ΔH in Table III

TABLE III

HEATS OF SOLUTION OF GASES IN ELASTOMERS
(Dynamic method)

Sulfur (%)	ΔH, cal./mole					
	Nitrogen	Methane	Ethane	Ethylene	Propane	Butane
1.7	0	−1000	−2650	−2700	−4000	−4700
2.9	0	−800	−2100	−2500	−4000	−5400
7.15	0	−1400	−2450	−2000	−3400	−5700
11.3	0	−1300	−2350	−2000	−3550	−5200
Butyl rubber	0	—	—	−900	−1900	—

are accurate to ±400 calories per mole due to the error of 200 calories per mole in the determination of E_P and E_D (see Part I). Values of ΔH for butane obtained by the dynamic method are in good agreement with those obtained by the static method, as is shown by Table IV, which lists values of ΔH for n-butane and for n-pentane according to the static method.

The effect of increasing the number of carbon atoms on ΔH is indicated by Figure 5, in which an apparent linear relationship is obtained. The higher numerical value of ΔH for butane, compared with the other gases, does not necessarily imply that liquid butane exhibits a greater affinity for rubber. ΔH may be divided into two quantities:

$$\Delta H = -L_t + q \qquad (2)$$

TABLE IV

HEATS OF SOLUTION OF GASES IN ELASTOMERS
(Static method)

Sulfur (%)	ΔH, cal./mole	
	n-Butane	*n*-Pentane
1.7	−4750	−6600
2.9	−5400	−6400
7.15	−5750	−6200
11.3	−5200	—
15.15	—	−6400

L_t is the total latent heat of vaporization and q is the heat of mixing of the liquefied gas with the elastomer. Now q is given by [13]:

$$q = [(E_1/V_1)^{\frac{1}{2}} - (E_2/V_2)^{\frac{1}{2}}]^2 V_1 v_2^2 \qquad (3)$$

where E_1 and E_2 are the cohesive energies of the condensed gas and elastomer, respectively; V_1 and V_2 are the corresponding molecular volumes; and v_2 is the volume fraction of the rubber.

From Tables III and IV it is clear that the heat of solution does not vary systematically with the degree of vulcanization. This indicates that the cohesive energy density of the rubber tends to be constant over the range of sulfur contents studied.

TABLE V

CALCULATED AND OBSERVED HEATS OF MIXING OF LIQUID GASES IN NATURAL RUBBER

Gas	E_1 (cal./mole)	V_1	(E_1/V_1)	q (cal./mole)	
				Calculated	Observed
Nitrogen	760 (−195° C)	32.8	4.8	+330	+1360
Methane	1620 (−159° C)	39.5	6.4	+95	+1100
Ethane	1660 (0° C)	54.4	5.53	+330	−200
Propane	3110 (20° C)	75.5	6.4	+180	−400
Butane	4500 (20° C)	98.5	6.8	+138	−150

In Table V experimental values of q (calculated from Equation 2) are compared with the theoretical values (Equation 3) assuming[6] that $(E_2/V_2)^{\frac{1}{2}} = 7.98$. Satisfactory agreement is obtained for propane, butane, and ethane, but a wide deviation is noted with nitrogen and methane. Nitrogen and methane are at the temperature of the experiment which is above their critical temperatures, making the hypothetical condensation process physically impossible; hence, E_1 has been obtained for a much lower temperature. E_1 is usually found to decrease with increasing temperature, and a lower value of E_1 for nitrogen and methane would reduce the difference in the experimental and calculated values of q. [See International Critical Tables (I.C.T.) for values of $l_v = L_t \times (4.18/\text{mol. wt.})$.]

FREE ENERGIES AND ENTROPIES OF SOLUTION

The solubility constant ρ may be defined as the ratio of concentration of gas in the rubber and gas phase. Accordingly the standard free energy for the process—gas dissolving in elastomer—is given by:

$$\Delta A_0 = -RT \ln \rho \qquad (4)$$

The standard state for the gas is taken as 76 cm. pressure and for the solution as that state in which the concentration of the gas is equal to the concentration in the gas phase.

The heats of solution in Table III have not been corrected for thermal expansion of the membrane. We may write[1]:

$$\Delta U_{net} = \Delta U + RT^2 \left(\frac{\delta \ln V_1}{\delta T} \right) \tag{5}$$

where V_1 is the molecular volume of the rubber[14], giving the values of ΔA_0, ΔU_{net}, and ΔS for natural rubber and Butyl tabulated in Table VI. These values may be compared with those in Table VII for the solution of nitrogen, methane, ethane, and ethylene in monomeric solvents (calculated from papers by Frank and Evans[15] and Horiuti[1]).

TABLE VI

FREE ENERGIES, NET HEATS, AND ENTROPIES OF SOLUTION OF GASES IN ELASTOMERS AT 60° C

Solvent	Solute	ΔA_0	ΔU_{net}	ΔS_0
Natural rubber	Nitrogen	+1740.0	+720	−3.07
	Methane	+787.0	−400	−3.56
	Ethane	−270.0	−1680	−4.25
	Ethylene	−110.0	−1580	−4.42
	Propane	−875.0	−3030	−6.17
	Butane	−1540.0	−4530	−9.00
Butyl rubber	Nitrogen	+1840.0	+720	−3.37
	Ethylene	+352	−180	−1.6
	Propane	−615	−1180	−1.68

TABLE VII

FREE ENERGIES, NET HEATS, AND ENTROPIES OF SOLUTION OF GASES IN MONOMERIC SOLVENTS AT 40° C

Solvent	Solute	ΔA_0	ΔU_{net}	ΔS_0
Benzene	Nitrogen	+1250	+1070 + RT'	+1.428
	Methane	+352.0	−270 + RT'	−1.00
	Ethane	−795.0	−2220 + RT'	−2.55
	Ethylene	−675.0	−2090 + RT'	−2.53
Chlorobenzene	Nitrogen	+1370	+680 + RT'	−0.2
	Methane	+505.0	−560 + RT'	−1.4
	Ethane	−690.0	−2360 + RT'	−3.35
	Ethylene	−563.0	−2130 + RT'	−3.00
Acetone	Nitrogen	+1040	+720 + RT'	+0.98
	Methane	+310.0	−270 + RT'	−0.17
	Ethane	−642.0	−2000 + RT'	−2.25
	Ethylene	−680.0	−2090 + RT'	−2.50

One may note that the partial molal entropy of solution in a monomeric liquid is given by:

$$\Delta \bar{S}_A = \Delta \bar{S}_c + R \ln \frac{1}{v_1} \tag{6}$$

$\Delta \bar{S}_c$ = partial molal entropy of condensation and v_1 = volume-fraction of the solute. The partial molal entropy of solution in a polymer is given by:

$$\Delta \bar{S}_B = \Delta \bar{S}_c + R \left[\ln \frac{1}{v_1} - v_2 \left(1 - \frac{1}{x} \right) \right] \tag{7}$$

when the solution is very dilute $v_2 \approx 1$ and if x is large:

$$\Delta\bar{S}_B = \Delta\bar{S}_c + R\left(\ln\frac{1}{v_1} - 1\right) \tag{8}$$

Thus the entropy of dilution of the polymer should always be more negative than that of dilution of the monomer by the term R. Tables VI and VII show that ΔS_0 for natural rubber is in fact almost always more negative than ΔS_0 for monomeric solvents; but the limit in the accuracy with which ΔU_{net} may be determined does not permit an accurate estimate of the difference.

STATISTICAL TREATMENT OF THE SOLUBILITY OF GASES

It has been demonstrated[5] that the isotherm for the solution of vapor in an elastomer can be represented by:

$$v_1 = \frac{p}{p_s}\left(1 - \frac{2}{Z}\right)^{Z/2} \tag{9}$$

where v_1 = volume fraction of vapor in the vapor–elastomer mixture; p = pressure of vapor above elastomer; p_s = saturated vapor pressure of the vapor; Z = coordination number of the solute in the rubber. Rearranging Equation (9), taking $\log_{10}$, and expanding, gives:

$$\log_{10}\frac{v_1 p_s}{p} = -\frac{1}{2.303}\left(1 + \frac{1}{Z} + \frac{4}{3Z^2} + \frac{2}{Z^3} + \cdots\right) \tag{10}$$

Neglecting terms involving powers of Z higher than the square, a quadratic in Z is obtained. Values of Z derived from the quadratic for butane in rubber (Table VIII) are of the expected order and agree very well with the values of

TABLE VIII

COORDINATION NUMBER (Z) FOR n-BUTANE IN NATURAL RUBBER

p (cm.)	p_s (cm.)	T (° C)	S (%)	σ	v_1	Z
76	118	10	1.7	33.1	0.148	3.12
			2.9	33.9	0.151	3.17
			7.15	41.7	0.186	5.06
			11.3	34.6	0.156	3.28
76	398.1	50	1.7	10.0	0.045	3.15
			2.0	10.5	0.047	3.4
			7.15	12.6	0.056	5.4
			11.3	10.3	0.046	3.27

4.0 (at 100° C) and of 3.53 (at 25° C) obtained by Barrer[5] from data for the benzene–rubber system, due to Gee and Treloar[16].

In the derivation of an expression for the solubility of a gas in an elastomer, Barrer has suggested that K in the relation:

$$K = \frac{v_1}{p\left[1 - \left(1 - \frac{1}{x}\right)\frac{2}{Z}v_2\right]^{Z/2}}$$

is given by one of the following expressions:

(*a*)
$$K = \frac{1}{kT}\left(\frac{kT}{2\pi m}\right)^{\frac{3}{2}}\frac{1}{\nu^3}e^{(-\Delta H + RT/2)/RT}$$

if no principal rotations of the dissolving molecule are converted to vibrations on solution;

$$(b) \qquad K = \frac{1}{kT}\left(\frac{kT}{2\pi m}\right)^{\frac{3}{2}} \frac{1}{\nu^4} e \left(\frac{kT}{8\pi^2 I_1}\right)^{\frac{1}{2}} e^{(-\Delta H+RT)/RT}$$

if one principal rotation is converted to a vibration;

$$(c) \qquad K = \frac{1}{kT}\left(\frac{kT}{2\pi m}\right)^{\frac{3}{2}} \frac{1}{\nu^5}\left(\frac{kT}{8\pi^2 I_1^{\frac{1}{2}} I_2^{\frac{1}{2}}}\right) e^{(-\Delta H+3RT/2)/RT}$$

if two principal rotations are converted to vibrations;

$$(d) \qquad K = \frac{1}{kT}\left(\frac{kT}{2\pi m}\right)^{\frac{3}{2}} \frac{1}{\nu^6}\left(\frac{kT}{8\pi^2 I_1^{\frac{1}{2}} I_2^{\frac{1}{2}} I_3^{\frac{1}{2}}}\right)^{\frac{1}{2}} e^{(-\Delta H+2RT)/RT}$$

if three principal rotations are converted to vibrations.

Values of ν have been calculated in cases (*a*), (*b*), (*c*), and (*d*) at $T = 333°$ K, taking $Z = 3.5$ and assuming for the moments of inertia:

(i) Methane $I_1 = I_2 = I_3 = 5.35 \times 10^{-40}$
(ii) Ethane $I_1 = I_2 = 42.4 \times 10^{-40}$; $I_3 = 11.03 \times 10^{-40}$
(iii) Ethylene $I_1 = I_2 = 30.0 \times 10^{-40}$; $I_3 = 5.7 \times 10^{-40}$
(iv) Propane $I_1 = I_2 = 50.0 \times 10^{-40}$; $I_3 = 100 \times 10^{-40}$
(v) Butane $I_1 = I_2 = I_3 = 100 \times 10^{-40}$

The calculated values of ν which give agreement with the observed solubilities are shown in Table IX.

Table IX indicates that there is a general tendency for ν to decrease as the molecular mass is increased. This has previously been noted by Barrer[5], who found that ν tended to be constant for the same gas in different elastomers.

TABLE IX[a]

Gas	v_1	ν	Case
Butane	4.6×10^{-2}	5.9×10^{11}	(*a*)
		5.0	(*b*)
		5.0	(*c*)
		5.0	(*d*)
Propane	1.2×10^{-2}	5.6×10^{11}	(*a*)
		5.6	(*b*)
		5.6	(*c*)
		5.4	(*d*)
Ethane	2.27×10^{-3}	5.8×10^{11}	(*a*)
		5.6	(*b*)
		5.80	(*c*)
		6.3	(*d*)
Ethylene	3.35×10^{-3}	6.25×10^{11}	(*a*)
		6.37	(*d*)
		6.5	(*c*)
		7.6	(*d*)
Methane	4.6×10^{-4}	7.5×10^{11}	(*a*)
		9.5	(*b*)
		10.7	(*c*)
		10.9	(*d*)
Nitrogen	8.8×10^{-5}	5.4×10^{11}	(*a*)

[a] An average value of v_1 is chosen for each gas in membranes containing 1.7, 2.9, 7.15, and 11.3 per cent sulfur.

SUMMARY

The solubility of nitrogen, ethylene, and the *n*-paraffins from methane to pentane has been measured in a series of natural rubber vulcanizates in relation to chain length of paraffin, temperature, and degree of cross-linking of vulcanizates which contain between 1.7 to 21.9 per cent combined sulfur.

For smaller, less soluble paraffins the degree of vulcanization had little influence on the solubility, but for higher molecular paraffins such as pentane this influence became significant. A qualitative interpretation of the effects observed is given. The solubility data are in all cases represented by a statistical theory of one of the authors for a mean frequency of vibration of the solute in the medium corresponding to the infrared (0.5 to 1.0 $\times$ 10^{12} sec.$^{-1}$). The solubility constants, σ, and critical temperature, T_c, are also empirically related by the equation:

$$\log_{10}\sigma = a + bT_c \ (a \text{ and } b \text{ are constants})$$

Heats and standard free energies of solution for the earlier homologous paraffins show steady trends as the chain length increases. The heats are exothermal, and are adequately interpreted as the sum of the heats of liquefaction, together with a small heat-of-mixing term for liquid and rubber, which was usually close to that given by Hildebrand's cohesive energy density equation:

$$q = [(E_1/V_1)^{\frac{1}{2}} - (E_2/{}^2V_2)^{\frac{1}{2}}]^2 V_1 v_2^2$$

As anticipated from statistical theory, entropies were usually several entropy units more negative than those for solutions of gases in monomeric solvents.

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REFERENCES

[1] Horiuti, *Sci. Papers Inst. Phys. Chem. Research Tokyo* **17**, 125 (1930).
[2] Lannung, *J. Am. Chem. Soc.* **52**, 68 (1930); Markham and Kobe, *Chem. Revs.* **28**, 519 (1941).
[3] Eley, *Trans. Faraday Soc.* **35**, 1283 (1939).
[4] Flory, *J. Chem. Physics* **9**, 660 (1941); **10**, 51 (1942); **12**, 425 (1944); **13**, 453 (1945); Huggins, *J. Phys. Chem.* **46**, 151 (1942); *J. Am. Chem. Soc.* **64**, 1712 (1942); Orr, *Trans. Faraday Soc.* **40**, 320 (1944) Guggenheim, *Proc. Roy. Soc. London* **A183**, 203 (1944); Alfrey and Doty, *J. Chem. Physics* **13**, 77 (1945); Scott and Magat, *J. Chem. Physics* **13**, 172 (1945); Scott, *J. Chem. Physics* **13**, 171 (1945).;
[5] Barrer, *Trans. Faraday Soc.* **43**, 3 (1947).
[6] Gee, *Quart. Revs.* **1**, 265 (1947).
[7] Barrer, *Trans. Faraday Soc.* **35**, 628, 644 (1939); **36**, 644 (1940); "Diffusion in and through Solids", New York, **1941**.
[8] Van Amerongen, *Rev. gén. caoutchouc* **21**, 50 (1944); *J. Applied Physics* **17**, 972 (1940); *J. Polymer Sci.* **2**, 381 (1947).
[9] Carpenter and Twiss, *Ind. Eng. Chem. Anal. Ed.* **12**, 99 (1940).
[10] Barrer and Skirrow, *J. Polymer Sci.* **4**, 549 (1948).
[11] σ is expressed in units of cc. of gas, measured at N.T.P. in 1 cc. of rubber, when the pressure of the gas is 1 atmosphere.
[12] Van Amerongen takes a value of 600 calories per mole for RT. This value is adopted in the present paper, since the error in taking this figure falls within the experimental error of approximately 400 calories per mole for ΔH.
[13] Hildebrand, "Solubility of Nonelectrolytes", New York, **1936**; Gee, *Quart. Revs.* **1**, 265 (1947).
[14] A value of 120 calories per mole is taken for the last term in (7). See Barrer, *Trans. Faraday Soc.* **35**, 628, 644 (1939); **36**, 644 (1940); "Diffusion in and through Solids", New York, **1941**.
[15] Frank and Evans, *J. Chem. Physics* **13**, 507 (1945).
[16] Gee and Treloar, *Trans. Faraday Soc.* **38**, 147 (1912).

THE DYNAMIC CHARACTERISTICS OF NEOPRENE VULCANIZATES

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The utilization of the elastomeric spring goes back at least to the days of solid rubber carriage tires. The use of such materials to dampen vibration or absorb shock expanded rapidly despite the lack of engineering data and the inadequacy of testing methods for proper evaluation. Within the last twenty years these materials have been used in many dynamic applications, even though no appropriate means existed for the measurement of dynamic properties to determine their suitability for the particular service. Coincident with the practical application of rubber parts to vibration problems, engineers developed considerable data on the use of natural rubber in springs.

Marked differences in performance were encountered when engineers were

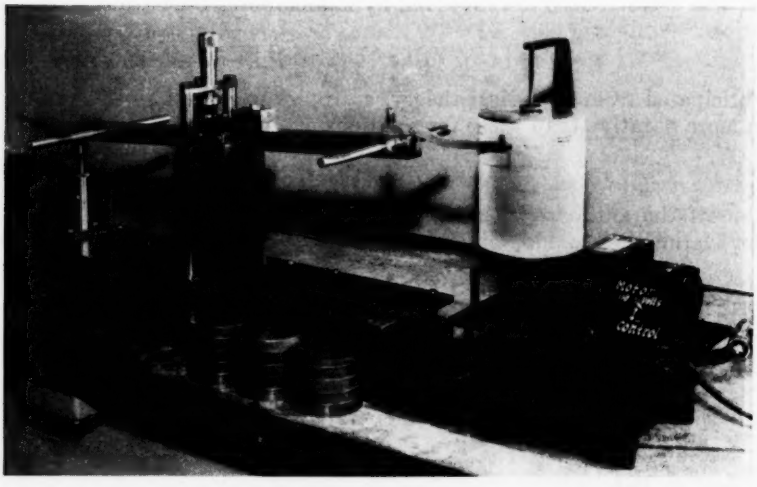

Fig. 1.

obliged to replace natural rubber with synthetic rubber in spring applications. Some engineers redesigned the rubber part used and obtained workable, although not entirely acceptable, performance. Design alone was not a complete solution to the problem, and it was necessary to call on the rubber technologist to produce vulcanizates having properties especially suitable for dynamic service.

In 1940 Yerzley[1] discussed the advantages of elastomeric springs over steel springs and pointed out certain advantages resulting from the use of Neoprene compositions in place of natural rubber. He showed that Neoprene vulcanizates possess greater damping and higher thermal conductivity than

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natural rubber. During the next five years, synthetic rubbers made vast gains in commercial importance, and the tempo of investigative development increased sharply, resulting in considerable gain in the general knowledge of their dynamic properties.

In 1945 Riesing[2] presented some general facts regarding both synthetic and natural rubber, and showed that tensile strength, elongation at break, and hardness were of little value in judging the merits of any elastomeric composi-

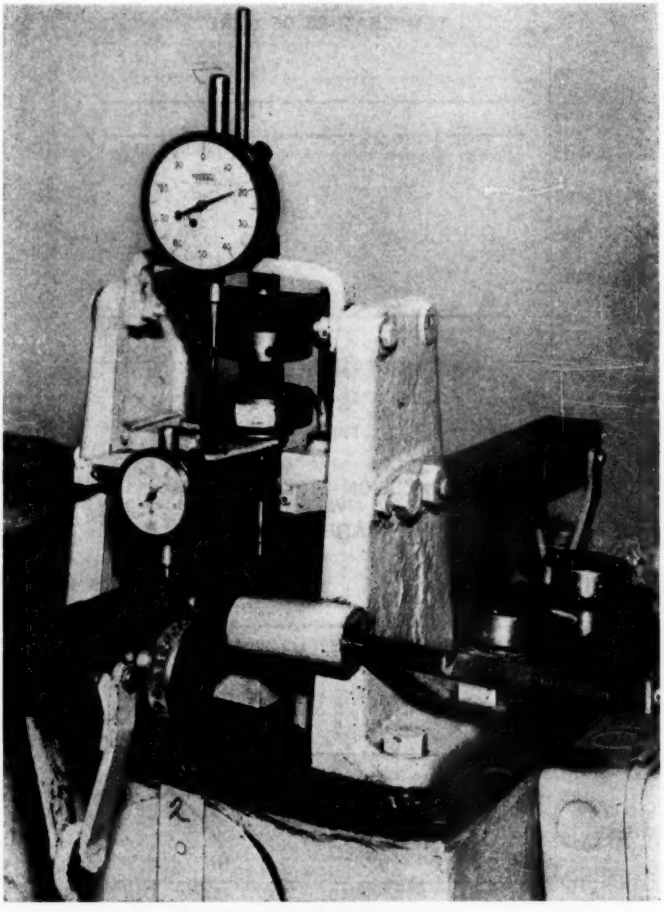

FIG. 2.

tion with respect to its ability to perform in mechanical parts. He indicated the need for improved methods of testing rubber in the low-strain range when loaded in compression, shear, or torsion.

In 1946 Morron[3] discussed many of the commonly measured properties of rubber. He compared the various synthetic rubbers with natural rubber, and again called attention to the inadequacy of usual static tests as a means of predicting the dynamic behavior of products made from these rubbers.

The development of synthetic rubber products and the accumulation of data describing their dynamic properties revealed that these vulcanizates were different from those made of natural rubber, and thus offered an opportunity to widen the field of application of elastic products in engineering.

The purpose of this paper is to discuss some of the dynamic characteristics of Neoprene vulcanizates and to show how they compare with similar stocks

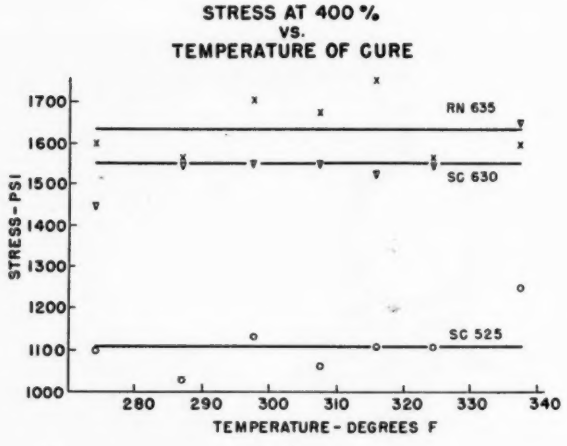

FIG. 3.

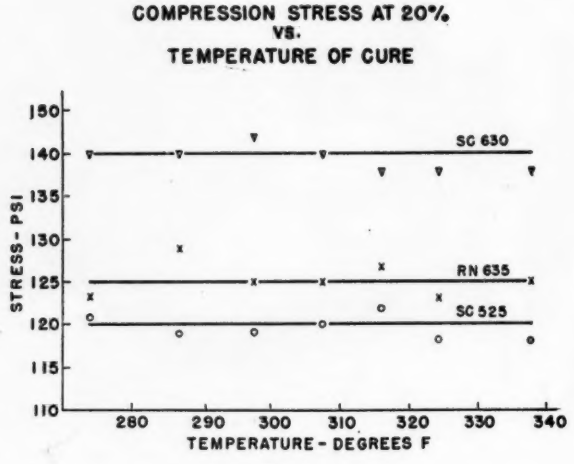

FIG. 4.

made from natural rubber. It is realized that the subject of dynamic characteristics is very extensive and one that has not yet been thoroughly explored in connection with synthetic rubber. Therefore, this paper is limited to a discussion of the effect of time and temperature of cure, of acceleration, of the temperature of testing, of variations in frequency and load, and of carbon black loading on some of the more important dynamic characteristics of Neoprene.

The du Pont-Yerzley oscillograph[4] (Figure 1) was used for measuring some of the mechanical properties of the compositions studied. It was operated in accordance with ASTM D945-48T. Measurements were made under both compression and shear loading.

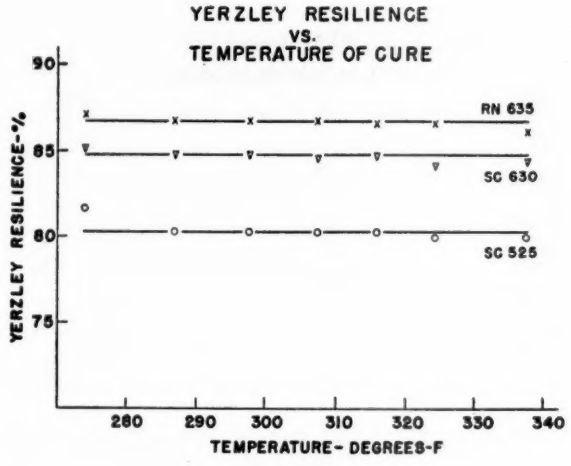

FIG. 5.

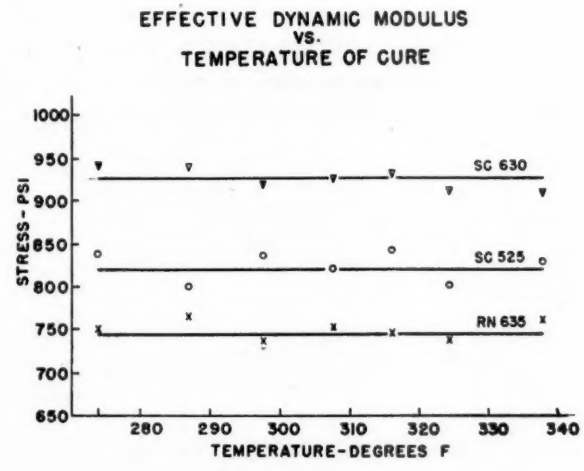

FIG. 6.

The Goodrich flexometer (Figure 2) was used in measuring the heat build-up of the compositions studied. The apparatus was operated in accordance with ASTM D623-41, using a $\frac{3}{16}$-inch stroke, a load of 150 lbs. per sq. in., and a frequency of 1800 cpm., with the following exceptions.

1. The use of dial gages to eliminate the necessity of reading a micrometer and to make leveling of the beam easier to follow.

2. The test specimen in the form of a truncated cone having a diameter at the top of 0.75 inch, at the bottom of 0.77 inch, and a height of 1 inch. Experience has shown that this test-specimen is superior to the one described in ASTM, since it is easier to prepare and further gives a simple 1-to-5 relationship between dead load and stress on the specimen.

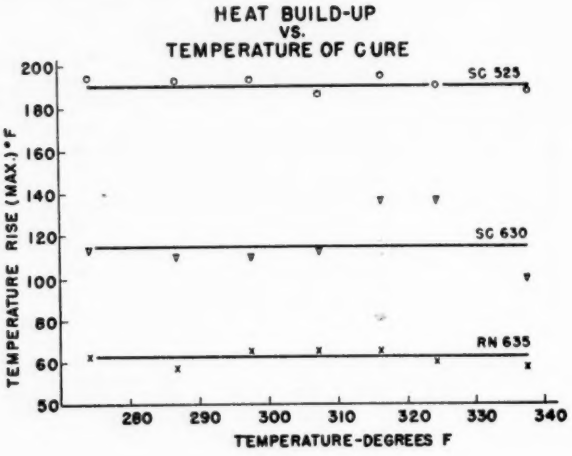

FIG. 7.

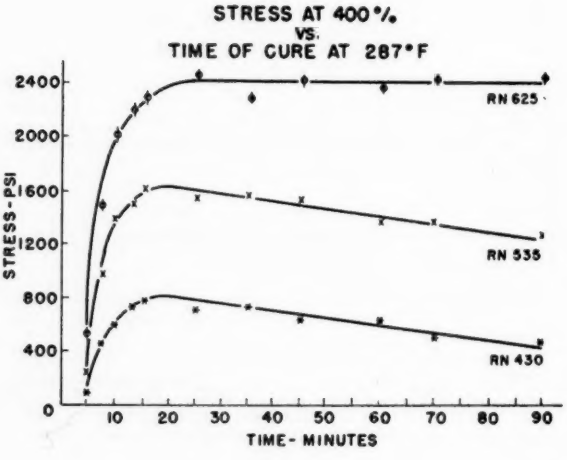

FIG. 8.

From the standpoint of the rubber technologist, it is of primary importance to know whether the temperature at which vulcanization is carried out has a significant effect on any of the dynamic properties of either Neoprene or natural rubber compositions. Temperatures ranging from 274° to 338° F at intervals equivalent to 10 lbs. per sq. in steam pressure were studied. At each of these

temperatures a time of cure was selected which produced equivalent states of cure as judged by modulus at 400 per cent and compression stress at 20 per cent strain. On the basis of these selections, samples were prepared with which compression oscillograms were made and heat build-up values were determined. The stocks chosen for this work were a rubber composition accelerated with

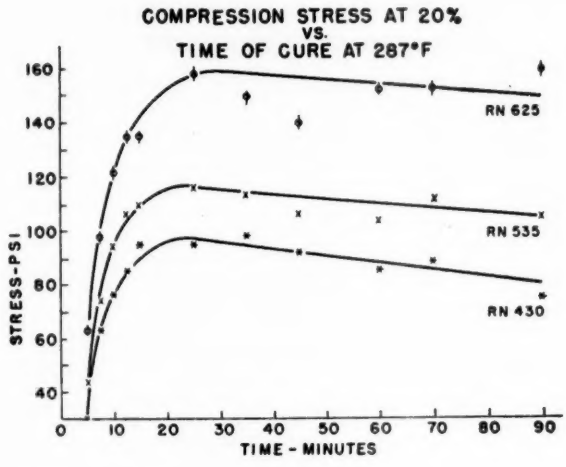

FIG. 9.

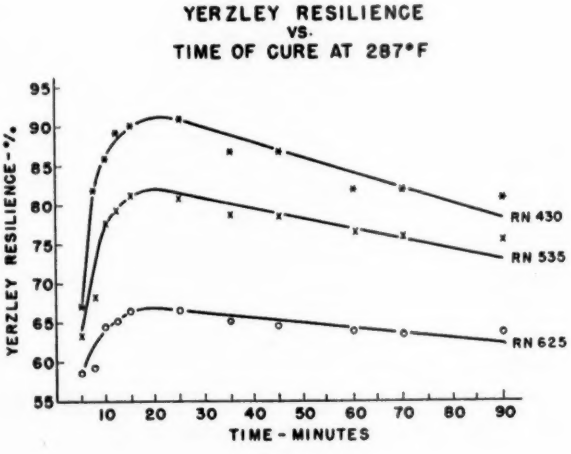

FIG. 10.

2-mercaptothiazoline, a Neoprene stock containing normal quantities of magnesium oxide and zinc oxide, and a Neoprene stock similar to the above except that it contained one part of antimony trisulfide. Each of these stocks contained 15 volumes of channel carbon black per 100 volumes of elastomer. Antimony trisulfide was selected as the accelerator for the Neoprene GR-M

stock on the basis of the work of Torrence[5], which revealed the advantages of this agent as a means of obtaining a high state of cure.

The results demonstrate that if equivalent states of cure are obtained as judged by tension modulus or by compression stress, the dynamic properties of the rubber and Neoprene vulcanizates are unaffected by the vulcanization

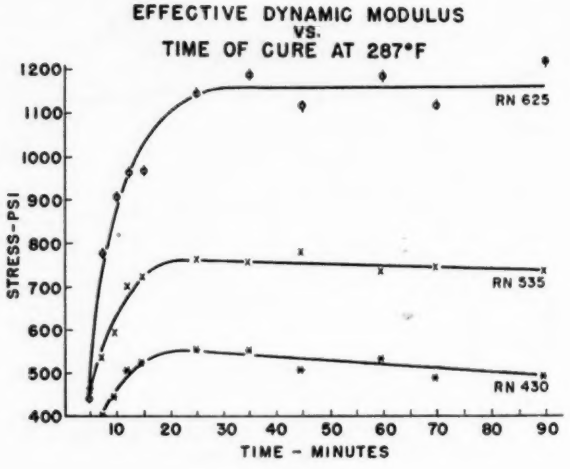

FIG. 11.

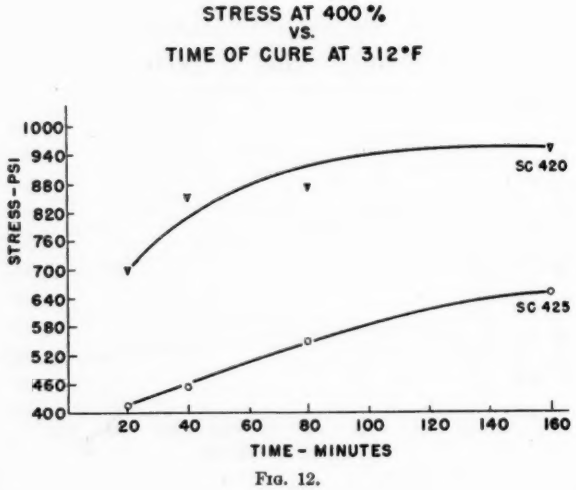

FIG. 12.

temperature. Figures 3 to 7 present in graphic form the results obtained with specimens cured at the various temperatures. In every case a horizontal, straight line can be drawn through the average of the results, showing that vulcanization temperature has no effect on the property studied. The points vary from this average no more than the normal expectancy of tests of this type.

The effect of time of cure at a given temperature on the dynamic properties of Neoprene and of rubber vulcanizates is shown graphically in Figures 8 to 15. At least within the limits of time of cure studied in this investigation, the Neoprene stocks behaved in a manner very different from that of the natural rubber stocks. With the Neoprene stocks there was no tendency to lose

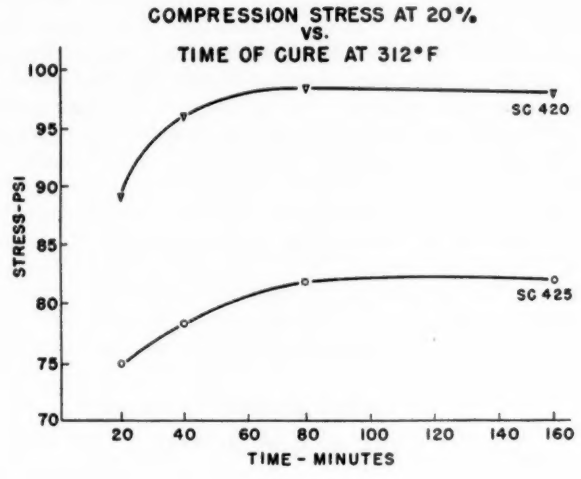

FIG. 13.

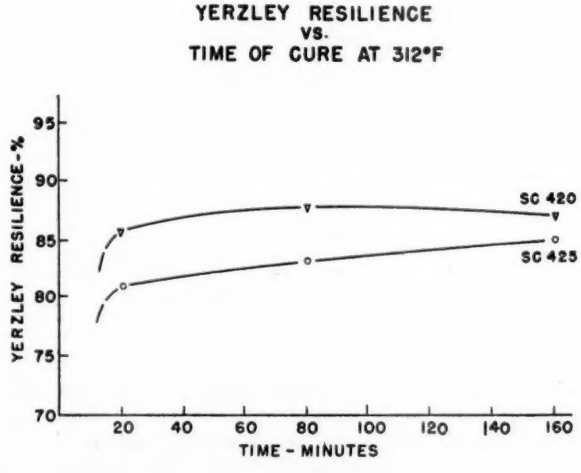

FIG. 14.

dynamic properties by long cure, whereas with the rubber stocks the well-established characteristic of falling off from optimum values by overcure is apparent. Figures 8 to 11 show the effect of curing time on the modulus, compression stress, resilience, and effective dynamic modulus of three different rubber stocks. Each of these stocks was accelerated with tetramethylthiuram

monosulfide, and was designed to meet the requirements for RN-430, 535, and 625. In each case the optimum value was reached in a curing time of approximately 25 minutes at 287° F. It should be noted that the loss in resilience by overcure is more evident than the loss in any of the other properties measured.

The effect of extending the time of curing on the dynamic properties of Neoprene stocks is demonstrated by Figures 12 to 15, where these properties of an accelerated (SC-420) as well as an unaccelerated (SC-425) Neoprene stock are shown graphically. It is noteworthy that, with the Neoprene stocks, more cure is necessary to reach the optimum values than was required for the rubber stocks; furthermore, the time of cure required varies more widely for the specific properties studied. On the other hand, long cures, up to 160 minutes at 312° F, did not result in any decrease from the optimum values. Composition SC-420 was accelerated with one part of Permalux[6]. Figure 12 shows that Permalux not only increases the stress considerably but decreases the time required to attain a high state of cure. The accelerating effect of Permalux is demonstrated further by the compression stress curves shown graphically in Figure 13. Figure 14 shows that the Permalux-accelerated stock (SC-420) reached its maximum resilience in much less time than the unaccelerated stock. The effective dynamic modulus shown graphically in Figure 15 closely parallels the tension modulus shown in Figure 8.

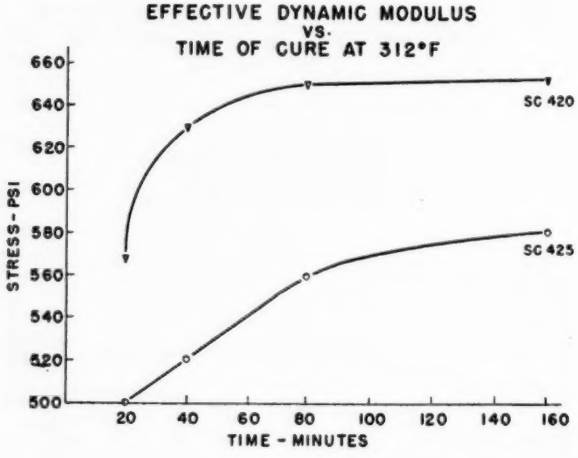

Fig. 15.

The literature on dynamic testing lacks sufficient data to enable the engineer to estimate with any degree of accuracy the effect of variations in testing conditions on the results obtained. Such testing factors as temperature of testing, variations in applied stress, and variations in frequency were therefore studied for some of the rubber and the Neoprene stocks already discussed.

The effect of temperature on dynamic properties was measured on a mechanical oscillograph which had its working section housed in a combination oven-coldbox capable of being operated over a wide range of temperatures so that temperatures other than room temperature could be maintained. Tests were conducted at temperatures ranging from 20 to 200° F. The results obtained are shown graphically in Figures 16 and 17. They do not permit gen-

eralization regarding the effect of temperature on dynamic properties. Figure 16 shows the effect of temperature on the compression stress of three Neoprene stocks (SC-420, 530, and 630) and three rubber stocks (RN-430, 535, and 625). It will be noted that the Neoprene stocks and the rubber stock containing the highest loading (RN-625) all tend to stiffen as the temperature is reduced.

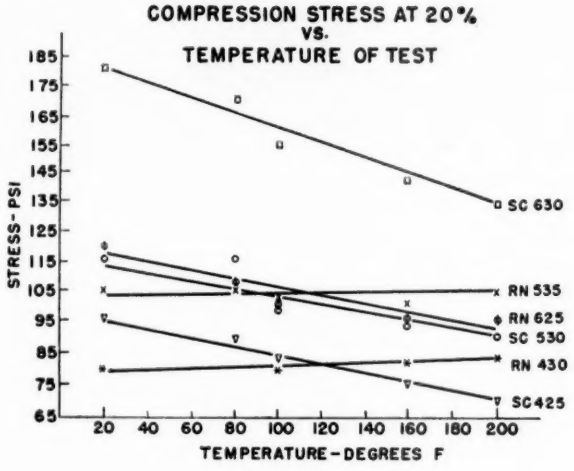

FIG. 16.

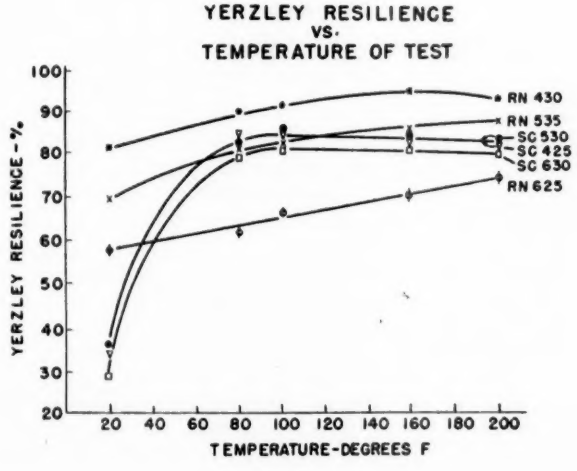

FIG. 17.

In the temperature range studied the compression stress of the rubber stocks containing the lower loadings (RN-430 and RN-535) was unaffected.

The effect of temperature on the Yerzley resilience of these same stocks is shown in Figure 17. As the temperature is increased from room temperature to 200° F, there is very little change in the resilience of either the Neoprene or

the rubber stocks. As the temperature is decreased below room temperature, both the Neoprene and the rubber stocks become less resilient. This change (probably associated with its higher freezing point) is much more marked with the Neoprene stocks.

The effect of variations in applied stress on the resulting heat build-up was investigated by the use of two Neoprene compositions (SC-525 and 630)

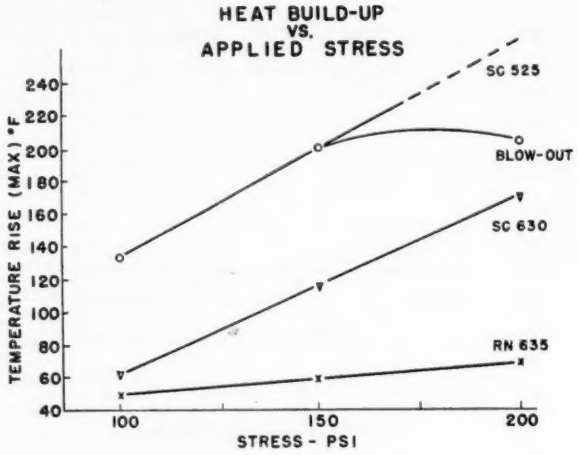

FIG. 18.

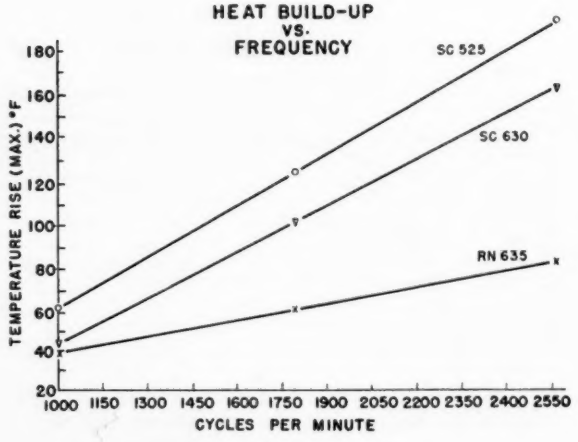

FIG. 19.

and on a rubber composition (RN-635). Figure 18 shows that an increase in applied stress results in a corresponding increase in heat build-up. Compositions SC-630 and SC-525 differ from each other only in the fact that the former was accelerated with one part of antimony trisulfide. It will be noted that the use of this accelerator reduced the temperature rise by approximately 70° F. The rubber stock (RN-635) was accelerated with 2-mercaptothiazoline, an

accelerator which is outstanding in producing stocks having a very low heat build-up.

The effect of variations in frequency of applied load on both heat build-up and Yerzley resilience was next investigated. Investigations of the effect of frequency on resilience were conducted in shear to eliminate the effects of slippage and shape factor[7]. The results are shown graphically in Figures 19 and 20. As the frequency is increased, the resilience decreases and the heat build-up increases at a uniform rate for both the Neoprene and rubber stocks.

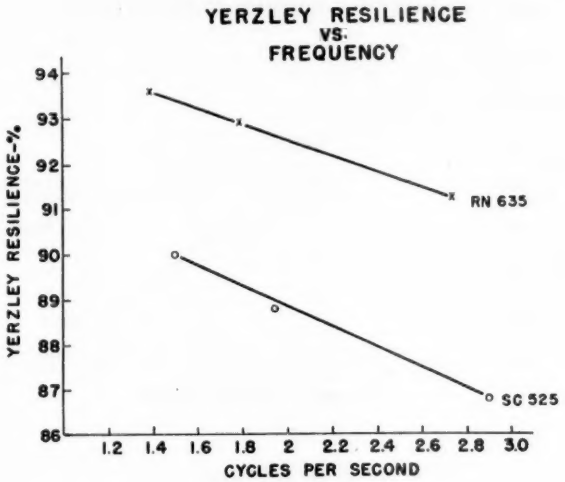

FIG. 20.

It has been well established that the properties of all elastomers can be markedly influenced by the choice and quantity of filler used in the compositions. Carbon blacks are the most widely used fillers in stocks designed for use in mechanical applications, and channel carbon black is generally used to impart the maximum tensile strength, resistance to tearing, and abrasion, and hardness for a given volume loading. However, it has long been recognized that the use of this filler leads to a marked decrease in resilience and an increase in heat build-up. Neoprene, like natural rubber, is reinforced by channel carbon black[8]. This was substantiated by Catton and Thompson[9], who measured the reënforcing effect of channel carbon black by studying its effect on the swelling of Neoprene vulcanizates by oil.

The effect of varying the loading of channel carbon black from 0 to 35 volumes per 100 volumes of elastomer (the practical compounding range for this type of black) on the Yerzley resilience, heat build-up[10], compression, and effective dynamic modulus of an antimony trisulfide-accelerated and unaccelerated Neoprene stock was studied. Rubber stocks accelerated with 2-mercaptothiazoline and having identical volume loadings of black were run as controls. The results obtained are shown graphically in Figures 21 to 24. In general, an increase in the volume-loading of black has the same qualitative effect on both Neoprene and natural rubber compositions. However, the quantitative differences are so great, particularly above the region of 12 to 18

volumes of black, that the absolute values of the various properties are often reversed. This points out in an unmistakable manner the danger of trying to adapt blindly information on natural-rubber compositions to those made from synthetic rubber. This variation is particularly evident in Figure 21, which shows the effect of increasing loadings of channel carbon black on the Yerzley resilience. It will be noted that, although the resilience of a gum

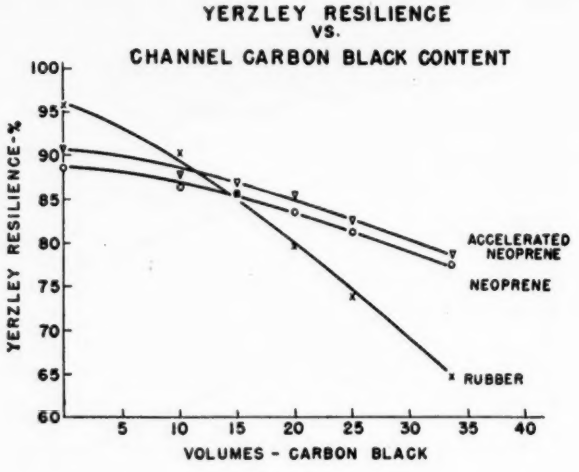

FIG. 21.

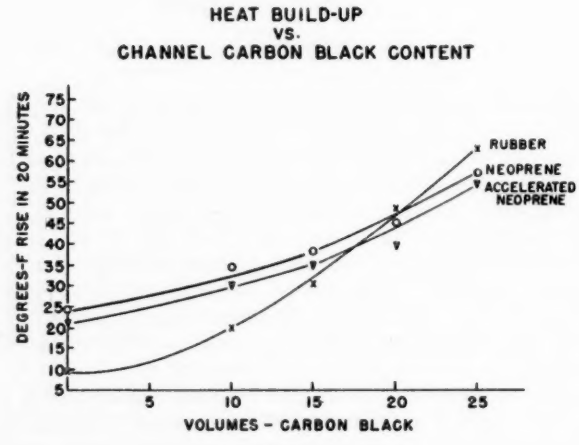

FIG. 22.

rubber stock is somewhat higher than that of a gum Neoprene stock (95 *vs.* 88 per cent), the loss in resilience on increasing the black loading is so much greater with rubber than it is with Neoprene that above 15 volumes the Neoprene stocks are the more resilient. At a loading of 25 volumes of channel carbon black the Neoprene stock has a resilience of 81 per cent, contrasted with only 73 per cent for the rubber stock. Since most stocks for mechanical applications contain

more than 15 volumes of carbon black, the data shown in Figure 21 are of particular importance in compounding for practical applications.

Figure 22, in which the effect of channel carbon black content on the heat build-up is plotted, shows the same characteristics as the figure on resilience already discussed. In the range of practical loading the Neoprene stocks show a lower heat build-up than the corresponding rubber stocks, even though the gum stocks show a marked superiority for rubber in this respect.

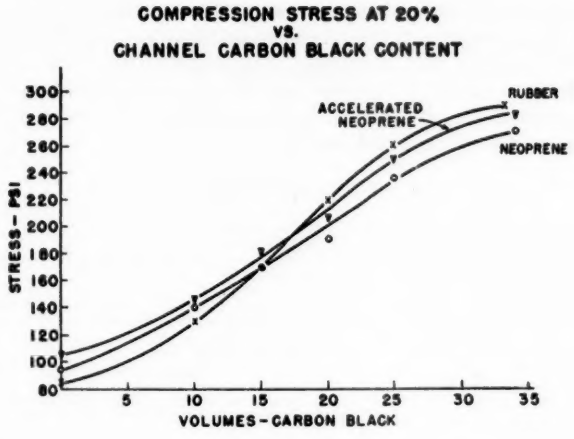

Fig. 23.

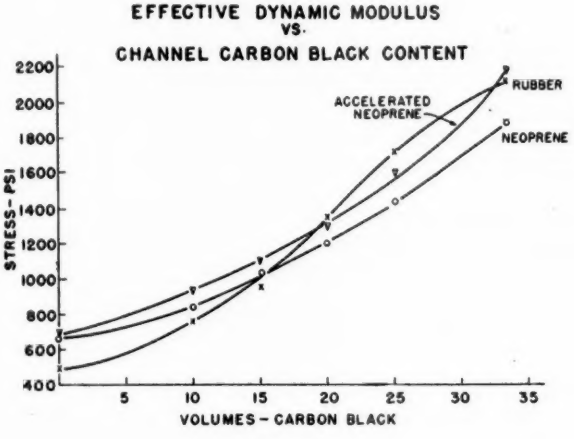

Fig. 24.

In the case of compression stress and effective dynamic modulus. Figures 23 and 24, the Neoprene stocks containing less than 15 volumes of channel carbon black are stiffer than the corresponding rubber stocks, whereas above this volume loading the Neoprene stocks are softer than their rubber counterparts. With these two properties, however, the change is not so great as it is in the case of resilience and heat build-up.

In all of the properties studied, the effect of accelerating the Neoprene stock is in agreement with the results to be expected from a higher state of cure, *i.e.*, higher resilience, lower heat build-up, higher compression stress, and higher effective dynamic modulus. The curves for these two Neoprene stocks are essentially parallel to each other, regardless of the property being studied.

It has been shown that the physical properties of natural rubber and Neoprene vulcanizates are unaffected by temperature of cure provided the resulting state of cure is the same. The dynamic properties of natural rubber stocks show characteristic reversion on extended curing at a given temperature which is not characteristic of Neoprene vulcanizates. Variations in frequency and load affect rubber and Neoprene vulcanizates in a like manner. Most important, the dynamic properties of Neoprene vulcanizates, particularly resilience, are not so greatly affected by the addition of increased proportions of carbon black as those of natural rubber.

REFERENCES

[1] Yerzley, "Neoprene as a Spring Material", *Am. Soc. Mech. Eng. Trans.*, July 1940.
[2] Riesing, *India Rubber World* 112, 59, 66, 186, 313 (1945).
[3] Morron, "The Evaluation of Rubber and Rubberlike Materials", presented at the meeting of the American Society of Mechanical Engineers, Detroit, June 1946.
[4] Yerzley, *India Rubber World* 100, 43 (1939).
[5] Torrence, "Vulcanization of Neoprene with Antimony Trisulfide", presented at the meeting of the Division of Rubber Chemistry of the American Chemical Society, Chicago, June 1948.
[6] Permalux is the di-*o*-tolylguanidine salt of dicatechol borate.
[7] Kimmich, "Rubber in Compression", *ASTM Bull.*, Oct. 1940.
[8] Columbian Carbon Company Research Laboratories, "The Carbon Reënforcement of Neoprene-GN", Columbian Colloidal Carbons, Vol. 6, No. 1.
[9] Catton and Thompson, "The Effect of Carbon Blacks on the Swelling of Neoprene GRM-10 Vulcanizates", presented at the meeting of the Division of Rubber Chemistry of the American Chemical Society, Cleveland, May 1947.
[10] In this particular test, a $\frac{1}{4}$-inch stroke was used instead of the $\frac{3}{16}$-inch stroke used elsewhere in this paper.

EFFECT OF LIGHT ON NEOPRENE. I. DISCOLORATION OF GR-M VULCANIZATES BY DIRECT SUNLIGHT *

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INTRODUCTION

Recent publications[1] concerned with the deterioration of vulcanized elastomers during exposure to weathering by either natural or artificial agencies are devoted primarily to studies of such effects as loss of tensile strength and development of exposure cracking. The discoloration of white or light colored natural-rubber vulcanizates during exposure to light is not considered a major problem, since the extent of discoloration is not great; and in many applications, such as white sidewalls for tires, the volume of white pigment is sufficient to hide any discoloration that might occur.

With GR-M the situation is the opposite as far as the importance of the problem is concerned. The outstanding resistance of properly compounded GR-M vulcanizates to loss of tensile strength or exposure cracking under weathering conditions has been well established[2], but the problem of discoloration is encountered with light colored or white vulcanizates. The latter is not surprising, since chlorine-containing polymers, whether unsaturated or not, are subject to discoloration by light[3].

When loss of tensile strength or exposure cracking of various vulcanized elastomers has been used as a criterion of degradation, the results of aging in artificial weathering devices have not shown correlation with those observed after exposure to natural conditions. In view of this, workers have been forced either to modify present accelerated aging equipment[4] or to construct entirely new weathering units[5].

It was the purpose of the present work to determine to what extent standard accelerated light-aging devices can be used to predict the resistance of white GR-M vulcanizates to discoloration by direct sunlight.

EXPERIMENTAL PROCEDURE

Recipe

The following compounding formula was used for white vulcanizates:

GR-M	100
Stearic acid	0.5
Rubber Blue GD	Variable*
White pigment	Variable
Extra light calcined magnesium oxide	4
Circo light process oil	1
Zinc oxide	5

* 0.1 Parts with each 20 parts of white pigment.

* This paper was presented before the Division of Rubber Chemistry at the 113th Meeting of the American Chemical Society, Chicago, Illinois, April 21–23, 1948.

Cures

Unless otherwise specified, all stocks were cured for 10 minutes at 60 lbs. per sq. in. steam pressure (307° F). Any variations from this cure are indicated.

Measurement of discoloration

Exposure of a white GR-M surface to light and oxygen results in the formation of chemical structures which tend to absorb visible light predominantly in the blue-violet region of the spectrum. The color changes accompanying this deterioration can be followed by determining the light reflectance of the surface over the visible spectrum; *i.e.*, 4000 to 7000 Å, before and after exposure[6]. This is shown in Figure 1, in which the progressive discoloration of a GR-M stock from white to brown during exposure to a weathering device is illustrated by reflectance curves. Light reflectance measurements were obtained with a Bechman spectrophotometer, using magnesium oxide as the standard.

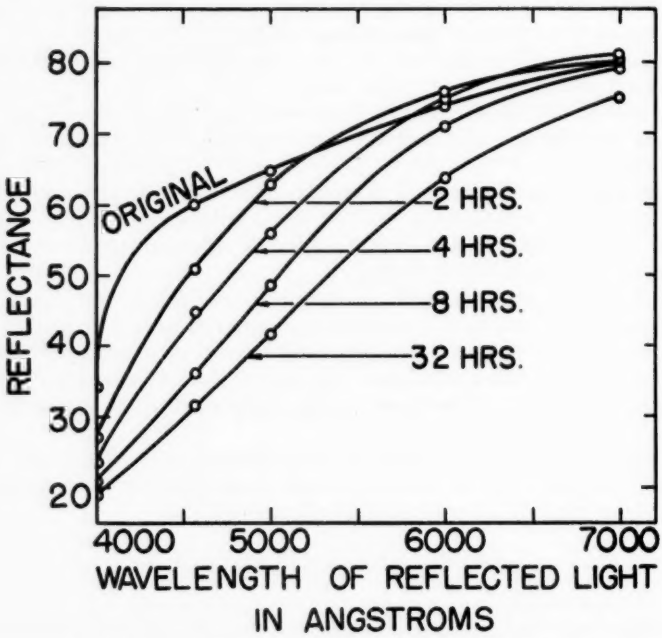

FIG. 1.—Discoloration of GR-M (20 TiO_2) by the weathering unit.

A simpler method for indicating changes in color, and one that is often applicable for determining both the rate and extent of discoloration of a GR-M vulcanizate, is to measure the reflectance at 4570 Å (monochromatic blue). This method measures the degree of yellowing, or discoloration, by the loss in reflectance in the blue portion of the spectrum. The loss of reflectance at 4570 Å correlates well with the observed discoloration when changes in reflectance during exposure to light in the red end of the visible spectrum are comparatively minor or follow a constant pattern of change. Thus the rate and extent

of discoloration of the vulcanizate shown in Figure 1 could have been illustrated by plotting the change in 4570 Å reflectance against time of exposure. Curves of the latter type are referred to in this paper as discoloration curves. The determination of the reflectance at 4570 Å is a standard method in the paper industry for comparing the relative whiteness of papers[7].

Measurements of the reflectance at 4570 Å for determining the discoloration by light of GR-M vulcanizates have, however, been found to be most useful with stocks cured for comparatively short times, *e.g.*, 10 minutes at 307° F. GR-M stocks darken during extended cures; and while such specimens discolor during exposure to sunlight, the yellowing results, not from a decrease in reflectance at 4570 Å, but from an increase in the reflectance in the green and red portions of the spectrum. An example of this is given in Figure 2 by the reflectance curves after one week in Florida of stocks cured 10, 30 and 60 minutes at 307° F. Judging only from measurements at 4570 Å on the stock cured for 60 minutes, it might be concluded falsely that the sample had become whiter.

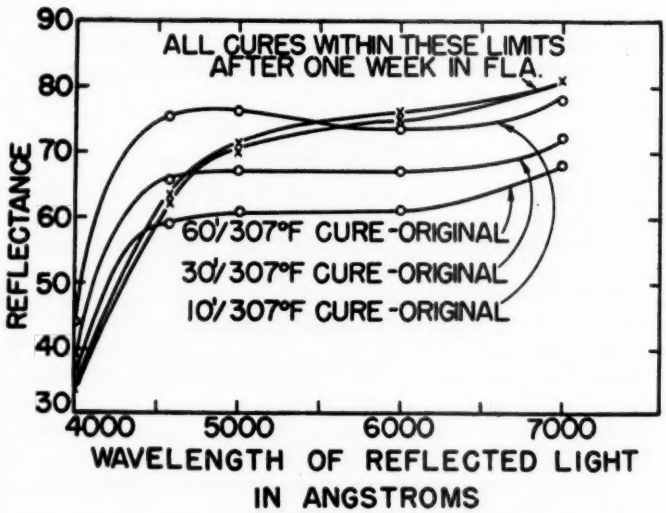

FIG. 2.—Effect of curing time upon discoloration of GR-M—80 PTS. TiO_2.

Exposure tests

Outdoor exposures to direct sunlight were carried out at Hialeah, Florida, and Woodstown, New Jersey. The samples were mounted at an angle of 45 degrees on racks facing south. The times of exposure given indicate total outdoor exposure. No attempt was made to determine the amount of sunlight that any sample received during the exposure. Weathering tests in Florida were conducted through the entire year and in New Jersey during the summer months. The results obtained in the outdoor exposures were undoubtedly influenced to a great extent by the particular climatic conditions during exposure, such as amount and intensity of sunlight, amount of precipitation, temperature, etc. Comparisons of samples should be made, therefore, only in those cases where the samples were exposed at the same time.

Artificial weathering tests were made with a National Carbon Company

Accelerated Weathering Unit, Model X-IA[4], equipped with "Sunshine" carbons and a water spray as specified by the A.S.T.M.[8] This apparatus is referred to as the "weathering unit". All radiation below 2600 Å was eliminated by Corex-D filters. The test-pieces, held approximately 19 inches from the arc in a cylindrical framework with a 2 hour rotation cycle, were always hung at the same level to avoid variations in discoloration resulting from differences in position in the unit[9].

Tests were also carried out in the above unit in the absence of the water spray. The apparatus in this case is referred to as the "NCC lamp".

A third series of accelerated light-aging experiments was carried out with a sunlamp equipped with a General Electric Type S-I bulb[10]. The specimens were placed for exposure approximately 19 inches from the light source.

Procedure

Exposures were carried out on pieces 1.5 × 1.5 × 0.075 inches, a convenient size for spectrophotometric measurements. The surfaces of samples exposed outdoors were washed with water to remove any adhering dirt. After exposures of two months or longer, some chalking of the pigment occurred, and this was also removed by water washing before reflections were determined.

ACCELERATED LIGHT AGING

The rate of discoloration of GR-M white stocks in the NCC lamp is extremely rapid during the first few hours and then levels off; the rate and extent of discoloration are determined by the amount of titanium dioxide pigment in the stocks. This is illustrated in Figure 3 by the discoloration curves of stocks with 20 and 80 parts, respectively, of pigment. After 16 hours' exposure, the stock with 20 parts of pigment had discolored to a deep, chocolate brown; that with 80 parts of pigment, to a somewhat lighter brown.

In the weathering unit, the rate and extent of discoloration of the above stocks are much less than in the NCC lamp, as shown in Figure 3. After 16 hours' exposure in the weathering unit, the stock with 20 parts of pigment was a yellow brown and that with 80 parts of pigment was cream colored. The

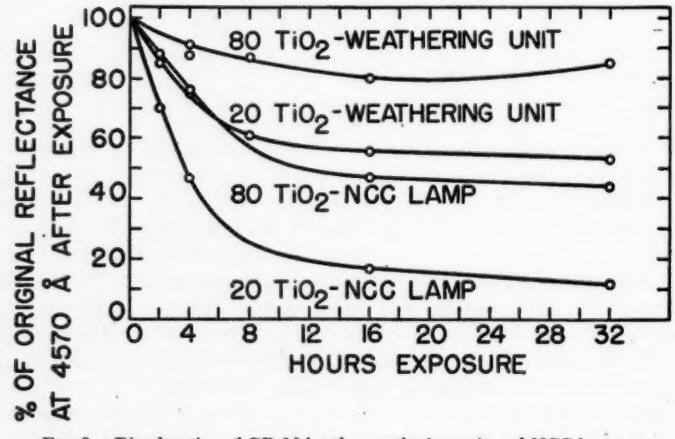

FIG. 3.—Discoloration of GR-M by the weathering unit and NCC lamp.

lower rate and degree of discoloration in the weathering unit compared with the discoloration in the NCC lamp may be due to any one or a combination of such factors such as the diminished light intensity under the water spray[9], the lower temperature of aging in the weathering unit[9], or the washing away of soluble oxidation products by the water spray[5].

The stock containing 20 parts of pigment was also aged in Florida for periods up to 24 weeks and under the sun lamp up to 30 days. The discoloration of this stock during exposure to Florida sunlight and accelerated light-aging devices is illustrated by curves in Figure 4.

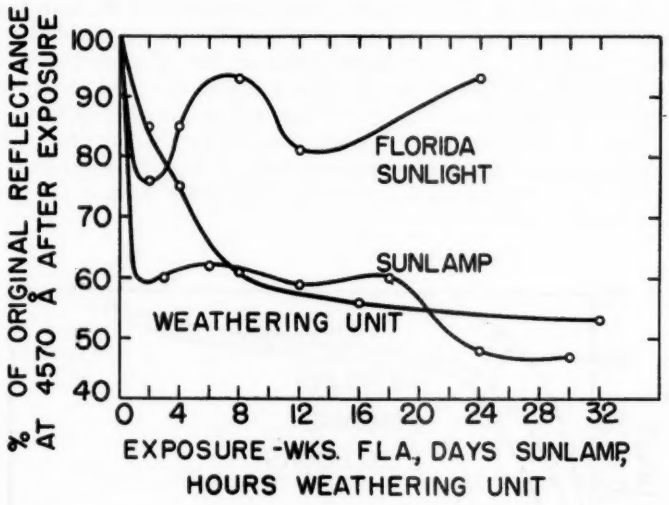

FIG. 4.—Discoloration of GR-M by various light sources—20 TiO_2 vulcanizate.

The effects produced by Florida sunlight differ from those produced by the weathering unit, the NCC lamp, or the sun lamp. Although GR-M discolors during the first few weeks in sunlight, it bleaches considerably during subsequent exposure. If the aging period in any of the light appliances is too long, a degree of discoloration results which is greater than that observed at any time during an exposure of 24 weeks in Florida. It can be concluded, therefore, that the light stability of GR-M white stocks is satisfactory for many uses, although this is not indicated by the accelerated light-aging tests commonly employed.

The behavior of samples under the sun lamp might be considered to fall in between that during outdoor exposure and that during aging in the weathering unit. The rapid initial yellowing, followed by bleaching, was observed to some extent with the sun lamp samples, but the degree of discoloration was greater than that of the Florida samples. Considering that no water spray was used with the sun lamp, which probably would have decreased both the rate and degree of discoloration, it appears possible that an apparatus, such as that designed by Kemp and Crabtree[5], which utilizes General Electric Type S-I and S-4 bulbs in conjunction with a water spray, might very well give excellent correlation with natural exposure.

NATURAL SUNLIGHT AGING

The discoloration curves in Figure 4 indicate broadly some of the differences in the type of discoloration produced by standard accelerated light-aging devices and that by direct sunlight. A consideration in more detail of the behavior of GR-M white stocks during sunlight exposure will further emphasize these differences, since a simple discoloration curve describes inadequately the discoloration of GR-M stocks during outdoor exposure.

As previously mentioned, GR-M stocks become increasingly more gray as the curing time is extended (Figure 2). During the first few hours in direct sunlight, the surface of GR-M stocks bleaches considerably, owing to the action of sunlight and air on the gray colored components formed during vulcanization. As illustrated in Figure 5, bleaching is very noticeable through the first 26 hours outdoors. On continued exposure for 22 more hours, however, the blue-white color of the bleached surface disappears and is replaced by a slight yellow discoloration. The bleaching action is believed to result from a combination of sunlight and air, since samples exposed in stoppered Pyrex brand flasks in an atmosphere of nitrogen exhibit no bleaching until the nitrogen is replaced by air. Furthermore, specimens aged in the dark in the presence of air do not bleach.

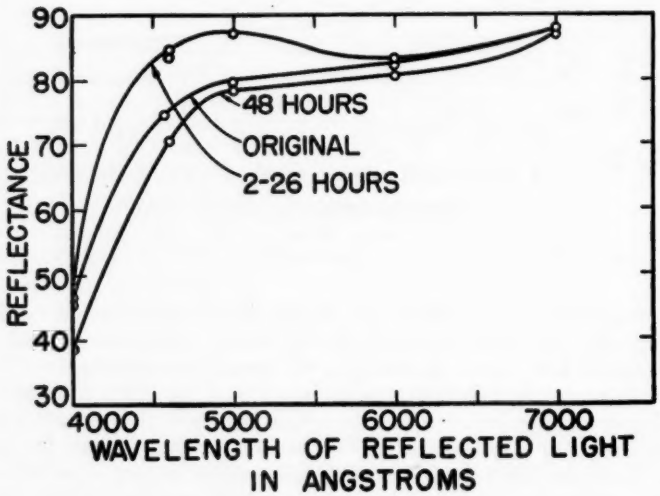

FIG. 5.—Initial bleaching of GR-M during sunlight exposure.

Once discoloration has started, it proceeds more or less steadily until the surface is a distinct yellow. This generally occurs within the first two weeks in Florida, but may take a month, depending on climatic conditions. Thereafter the surface bleaches, the yellow color fades, and the color of the stock becomes lighter. Possibly this is because the structures responsible for the yellow color are themselves partially destroyed by oxidation as exposure continues. Figure 6 shows the discoloration during an exposure of 24 weeks in Florida of a GR-M stock containing 20 parts of titanium dioxide. The fading of the yellow discoloration throughout the exposure from 2 to 8 weeks is indi-

cated by the progressive increase in reflectance in the blue region of the spectrum during this time. On continued exposure from 8 to 12 weeks, the surface again discolored and darkened. However, the loss in light reflectance was not confined so predominantly to the blue-violet region as during the first two weeks of exposure, but extended more into the green and red. Consequently, the surface was considerably less yellow than after the first two weeks of exposure and tended instead toward a gray-brown discoloration. After 24 weeks' exposure, the surface was even less discolored than after 12 weeks. As shown in Figure 6, the surface then reflected more light in the blue region than after 12 weeks and had become more gray than brown.

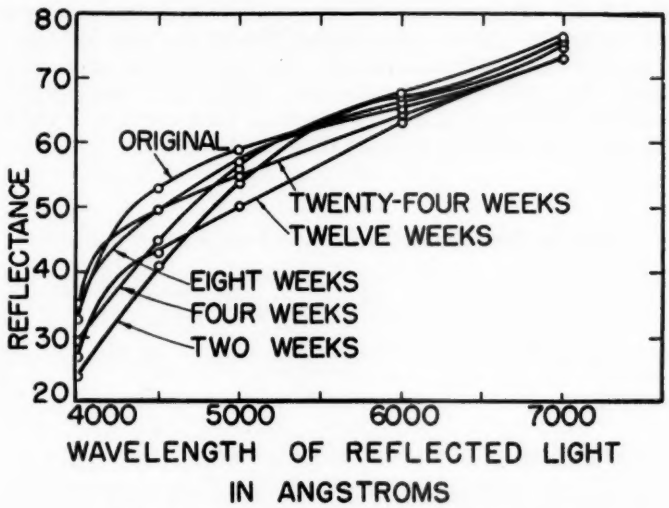

FIG. 6.—Sunlight discoloration of GR-M—20 PTS. TiO_2.

The preceding sections have demonstrated the difference between the effect of sunlight and the effect of accelerated light-aging devices on a GR-M stock compounded with 20 parts of titanium dioxide pigment. In sunlight the surface alternately bleached and discolored during outdoor exposure, with the color tending to proceed from white to yellow to yellow brown and finally toward gray. The degree to which these surface changes take place in sunlight is undoubtedly influenced by climatic conditions, but the behavior of GR-M in sunlight is also influenced by other variables, such as time of cure and type and proportion of white pigment utilized in compounding. To obtain a more complete understanding of the action of sunlight on GR-M, it is necessary to consider the effect of these variables.

Variation in white pigment

The titanium dioxide pigments as a class are the best and most widely used for the compounding of GR-M white stocks. However, the titanium dioxide pigments differ among themselves in the degree of stability conferred upon GR-M, partially at least, as a result of a difference in crystalline form. As shown in Table I, stocks compounded with the rutile crystalline form of

TABLE I

EFFECT OF VARIATION IN TITANIUM DIOXIDE PIGMENTS

Crystalline form	Percentage retained reflectance at 4570 Å after exposure in New Jersey	
	1 Week	2 Weeks
Rutile	81	86
Anatase	75	72

titanium dioxide are appreciably more stable to light than those with the anatase crystalline form.

Pigments other than titanium dioxide have an adverse effect on the light stability of GR-M. The decreased light stability of stocks compounded with zinc sulfide or TiCAL (30 per cent rutile TiO_2-70 per cent calcium sulfate) compared to that of a stock compounded with rutile titanium dioxide is indicated in Table II. The differences in the reflectance of the rutile stocks in Tables I and II exposed for the same length of time are due to the fact that they were exposed at different times in different localities.

TABLE II

EFFECT OF ZINC SULFIDE AND TiCAL ON LIGHT STABILITY

Pigment (40 parts)	Percentage retained reflectance at 4570 Å after exposure in Florida		
	1 Week	2 Weeks	4 Weeks
Rutile titanium dioxide	77	80	86
TiCAL	61	61	75
Zinc sulfide	57	43	40

Variation in proportion of titanium dioxide pigment

As the proportion of titanium dioxide pigment in a stock is increased, the alternating bleaching and discoloration during outdoor exposure becomes less pronounced. This might be expected, since the increased proportion of pigment covers up color changes more than lesser proportions of pigment; furthermore the surface contains less GR-M, the material, that is, bleaching and discoloring. The effect of a variation in titanium dioxide from 20 parts to 80 parts on the behavior of a GR-M stock during 24 weeks exposure in Florida is shown in Figure 7.

Effect of time of cure

Increasing the curing time affects only the initial color of the vulcanizate and not the stability in sunlight. As indicated in Figure 2, GR-M stocks discolor, not only in sunlight, but also during cure; and the degree of discoloration during cure depends on the time of curing. The discoloration during curing differs, however, from that observed in sunlight in that in the former case, the vulcanizate merely becomes increasingly more gray, while in the latter, it becomes yellow. The gray color developed during curing is evidently destroyed by exposure to sunlight and air, since, as shown in Figure 2, all stocks have the same reflectance curve after one week in Florida, regardless of the initial cure and color. On continued exposure, the light stability of the vulcanizates is practically identical, as shown in Figure 8.

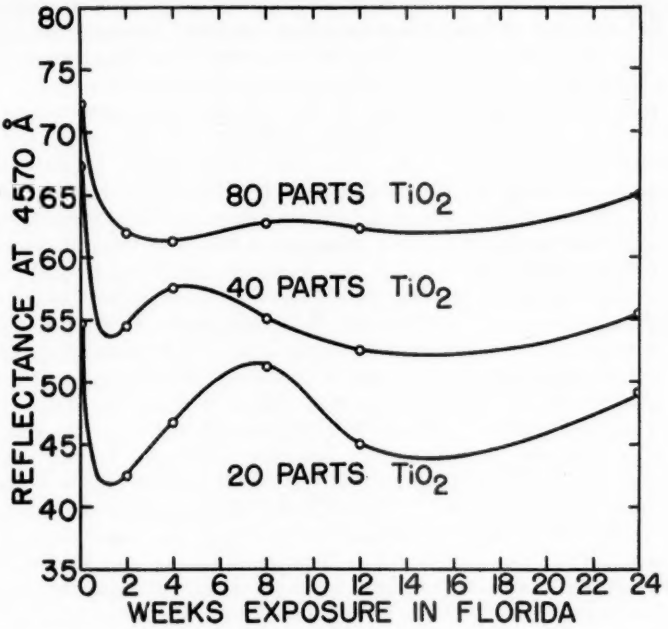

FIG. 7.—Sunlight discoloration of GR-M with varying amounts of TiO_2.

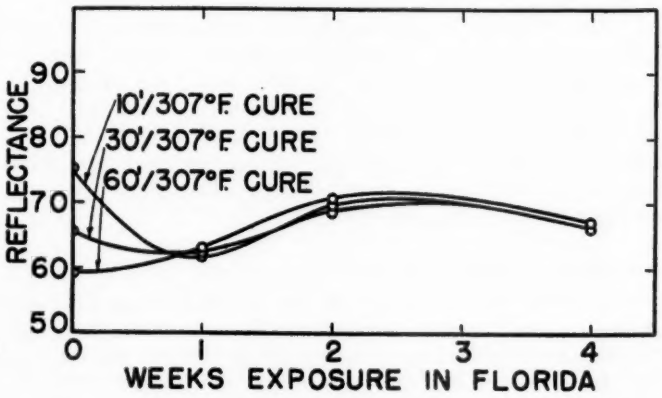

FIG. 8.—Effect of curing time upon discoloration of GR-M—80 PTS. TiO_2.

Relative sunlight stabilities as determined by accelerated tests

It has been shown that the behavior of a GR-M white stock during outdoor exposure cannot be predicted accurately by accelerated light tests. This, however, does not exclude the possibility of using accelerated light aging devices for preliminary screening purposes in a search for light stabilizers and nondiscoloring antioxidants, since a control with known sunlight stability can be included. To determine how useful accelerated light tests could be for this purpose, a series of vulcanizates, varying in their sunlight stability as a result of

the pigments and antioxidants used in compounding, were also aged in the accelerated devices. The differences in light stability between the control and the other stocks in the series after the accelerated light tests were then compared to those differences obtained by direct sunlight exposures.

The relative sunlight stabilities of the samples were determined after an exposure period of two weeks to direct sunlight. It was necessary to select some arbitrary aging period and two weeks was chosen because maximum yellowing usually occurred within this period. The differences in the percentage of retained reflectance at 4570 Å between the control and the other members of the series were assumed to be a measure of the relative sunlight stabilities.

The relative light stabilities of the samples according to the accelerated light tests were obtained by determining the difference in percentage of reflectance retained between the control and the other stocks at the point where the control became as discolored (had the same 4570 Å reflectance) as the sunlight control. The exposure time in the accelerated light-aging units when the control had discolored this amount was obtained from discoloration curves, such as those in Figure 3. The 4570 Å reflectance of the control after sunlight exposure was already known, and by applying this value to the discoloration curves from the accelerated light tests, the exposure time to reach this 4570 Å could be determined directly. The 4570 Å reflectances of the samples other than the control were then determined for the same exposure time.

By this method the differences in light stability by accelerated light tests and direct sunlight were determined for a series of vulcanizates, as discussed in the following sections. It can be concluded from the results that accelerated light aging tests indicate the various stocks to have a better light stability in comparison with the control than is observed after direct sunlight exposures. Rutile titanium dioxide stocks, for example, are much better than the corresponding anatase titanium dioxide stocks by accelerated light tests than they are by direct sunlight tests. Likewise, increasing the amount of titanium dioxide in a stock improves the light stability more according to accelerated light tests, than is observed in sunlight exposures. The same effect occurs with stocks containing antioxidants. Accelerated light tests indicate some antioxidants to be almost nondiscoloring, whereas sunlight tests show that the antioxidants cause considerable discoloration. The data from which these conclusions were drawn are as follows.

Variation in titanium dioxide pigment

A series of stocks compounded with 20, 40 and 80 parts of anatase and rutile titanium dioxides, respectively, were exposed to the various light sources. Stocks compounded with the anatase titanium dioxide were considered the controls for stocks containing an equivalent proportion of rutile titanium dioxide. No comparisons were made between vulcanizates with differing percentages of pigment. The improvement in light stability achieved by using rutile titanium dioxide instead of anatase titanium dioxide is shown in Table III.

With one exception (which may be an error), all evaluations by accelerated light tests indicated a higher degree of light stability for the rutile titanium dioxide specimens compared to the anatase stocks than is observed in sunlight.

Variation in amount of titanium dioxide

Increasing the proportion of rutile titanium dioxide in a GR-M stock increases the resistance of the vulcanizate to discoloration by direct sunlight, but

TABLE III

COMPARISON OF RUTILE WITH ANATASE TITANIUM DIOXIDE
(Anatase controls discolored to same amount in all tests)

	Percentage retained reflectance at 4570 Å							
	N. J. sunlight		Weathering unit		NCC lamp		Sun lamp	
Parts—TiO_2	Reflect.	Diff.	Reflect.	Diff.	Reflect.	Diff.	Reflect.	Diff.
20—Anatase	56	+7	56	− 2	56	+17.5	56	+10
20—Rutile	63		54		73.5		66	
40—Anatase	67	+6	67	+16	67	+18	67	+13
40—Rutile	73		83		85		79	
80—Anatase	72	+3	72	+14	72	+17	72	+18
80—Rutile	75		86		89		90	

TABLE IV

EFFECT OF VARYING AMOUNTS OF RUTILE TITANIUM DIOXIDE
(20 TiO_2 control discolored to same amount in all tests)

	Percentage retained reflectance at 4570Å							
	Florida sunlight		Weathering unit		NCC lamp		Sun lamp	
Parts TiO_2	Reflect.	Diff.	Reflect.	Diff.	Reflect.	Diff.	Reflect.	Diff.
20	76		76		76		76	
40	79	+3	86	+10	84	+ 8	82	+ 6
80	84	+8	92	+16	80	+13	88	+12

not as much as one would be led to expect from the results of accelerated light tests. The improvement in light stability when the titanium dioxide is increased from 20 to 40 to 80 parts in a stock is shown in Table IV.

Effect of antioxidants

The GR-M vulcanizates discussed in the preceding sections contained no added antioxidant. For most purposes the resistance of GR-M white stocks is sufficient without an added antioxidant (as a result of the tetraethylthiuram disulfide present as a stabilizer). For example, a GR-M vulcanizate compounded with 80 parts of titanium dioxide retained 50 per cent of its tensile strength and 40 per cent of its elongation after 14 days in the oxygen bomb at 70° C and 300 lbs. per sq. in. pressure of oxygen. After an exposure of 24 weeks in Florida the stock was also in very good condition. In the event, however, that the need for a nondiscoloring antioxidant should become more important, it was decided to determine the effectiveness of accelerated light aging tests for evaluating the discoloring characteristics of antioxidants. Stocks compounded with 40 parts of rutile titanium dioxide and 2 parts of various antioxidants were exposed in Florida, the NCC lamp, and the weathering unit. The light stabilities of the stocks containing antioxidants relative to that of the control with no added antioxidant are given in Table V.

Judging from the accelerated light tests, monobenzyl ether of hydroquinone and *p*-phenylphenol are almost nondiscoloring. They cause considerable discoloration in GR-M vulcanizates exposed to direct sunlight, however. Dixylenol butane retards the discoloration of GR-M vulcanizates during accelerated light aging tests but not during exposure to direct sunlight.

TABLE V

LIGHT STABILITIES OF VULCANIZATES WITH ANTIOXIDANTS
(Control discolored to same amount in all tests)

Antioxidant	Percentage retained reflectance at 4570 Å		
	Florida sunlight	Weathering unit	NCC lamp
Control (no antioxidant)	81	81	81
Dixylenol butane	78	90	88
Monobenzyl ether of hydroquinone	39	76	78
p-Phenylphenol	58	75	73
Phenyl-β-naphthylamine	15	21	41

DISCUSSION OF RESULTS

When accelerated light tests are of such duration that the controls are no more discolored than after exposure to sunlight, the tests indicate the various stocks to be relatively more stable with respect to the control than does exposure to direct sunlight. It can be considered, therefore, that under these circumstances accelerated light tests are more sensitive than is direct exposure to sunlight. In view of this, accelerated light-aging devices should be of considerable value in any program which involves the evaluation of potential light stabilizers and nondiscoloring antioxidants, since the chances of missing a promising lead are less than in direct sunlight tests.

CONCLUSIONS

1. White GR-M vulcanizates discolor differently in direct sunlight from what would be predicted from results obtained with standard light-aging devices.

2. Accelerated light-aging tests are of value for preliminary screening purposes if the control (of known stability to sunlight) is discolored to about the same extent as it would be by sunlight. Under these circumstances accelerated light tests indicate the other stocks to be relatively more stable with respect to the control than does exposure to direct sunlight.

3. Stocks most stable to light are obtained by using high proportions of the rutile crystalline form of titanium dioxide as white pigment. Variations in curing time affect only the initial color of the stock before exposure to light and not its resistance to discoloration by sunlight.

4. The results in this paper apply only to GR-M and to no other Neoprene, and only where outdoor exposures are involved. Preliminary results obtained by aging GR-M in indirect sunlight (behind glass) indicate that the effects produced by direct and indirect sunlight differ.

REFERENCES

[1] Morris, Hollister, Barrett, and Werkenthin, *Rubber Age* (N.Y.) **55**, 45 (1944); Newton, RUBBER CHEM. TECH. **18**, 504 (1945); Crabtree and Kemp, *Ind. Eng. Chem.* **38**, 378 (1946).
[2] Northam, Rubber Chemicals Division Report No. 38–2, E. I. du Pont de Nemours & Co., Feb. 1, 1938.
[3] Marvel, Jones, Mastin, and Schertz, *J. Am. Chem. Soc.* **64**, 2356 (1942); Boyer, *J. Phys. Colloid Chem.* 1, 80 (1947).
[4] Morris, Hollister, Barrett, and Werkenthin, *Rubber Age* (N.Y.) **55**, 45 (1944).
[5] Crabtree and Kemp, *Ind. Eng. Chem.* **38**, 278 (1946).
[6] Casey, *J. Chem. Education* **24**, 446 (1947).
[7] Tech. Assoc. Pulp and Paper Ind., Standardizing Procedure T452, SM-42.
[8] American Society for Testing Materials, A.S.T.M. Designation D750-43T (1946).
[9] Chatten and Werkenthin, *India Rubber World* **108**, 40 (1943).
[10] Ellis and Wells, "The Chemical Action of Ultraviolet Light", New York, **1941**, Chap. VIII.

A STUDY OF ELECTROSTATIC CHARGES PRODUCED DURING MASTICATION OF RUBBER AND OF GR-S*

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The production of static electricity during the mastication of rubber has been known for years. Static electricity[1] has, however, been considered primarily as a fire hazard, mechanical trouble in industrial processes, or as a source of radio interference; and relatively no work has been done relating electrostatic fields and contact potentials with the chemical and physical properties of the materials involved. This has been due in part to inadequate measuring equipment (Gold Leaf electroscope) and to the elusive nature of static electricity.

In a previous paper[2] a new apparatus (the electrostatic modulator) was described for measuring electrostatic contact potentials of cured rubber and GR-S; as a result of this work, an "electrostatic contact potential theory of reinforcement" was developed. In a subsequent paper[3] a relation between electrostatic contact potential and tensile strength at elevated temperatures for rubber and GR-S, helped to explain the extremely poor tensile properties of GR-S at elevated temperatures.

In the present paper, a new and improved electrostatic modulator is described. This electrostatic modulator records on a chart not only the electrostatic charge, or field strength, but also the polarity of the field. This device has been installed on a laboratory mill, and a study has been made of the changes in electrostatic fields produced by masticating rubber and GR-S. Electrostatic breakdown curves are shown which indicate that crude rubber starts with a highly negative field of −7000 volts. This drops down to 0 value, then may increase to +1500 volts as mastication proceeds. Since oxidation can be defined as a permanent loss of electrons, this loss of electrons, or electronic rearrangement, indicates an oxidation reaction. Regular GR-S on mastication does not show this great decrease in electrostatic charge. Low-temperature (14° F) polymerized GR-S (Philprene-B) starts out with a potential of 1500 volts, and this does not change as mastication proceeds, indicating little or no breakdown on milling.

A partial correlation of electrostatic field strength with Mooney viscosity is shown for both rubber and GR-S.

This apparatus has possibilities for processing control, inasmuch as a rough idea of plasticity can be obtained by the decrease in charge as mastication proceeds. Any change in mill gauge and cutting of the batch shows on the charge curve. Pigments and softeners, which will be covered in a subsequent paper, produces a marked change in the curve, which is specific for each ingredient.

* This paper was presented before the Division of Rubber Chemistry of the American Chemical Society at its meeting in Los Angeles, California, July 22–23, 1948.

The time on the mill, as well as the number of cuts preliminary to batching off, can be followed on the charge curve.

In general, the more negative the rubber, the better the dispersion and the faster the rate of incorporation of positive pigments or other positive compounding ingredients. The greater the difference in electrostatic potential between the rubber and compounding ingredient, the greater the attractive force between them and, consequently, the faster the incorporation of the added ingredient. If the rubber is masticated too long, it becomes soft, and the electrostatic field becomes positive (+); dispersion is thus rendered difficult because of repulsion of the positive fields around the rubber and the pigment.

With this device, not only can a check be made on a mill operator's mixing procedure; but fundamental studies can be carried out on the incorporation of pigments and softeners, thus assuring the proper timing and sequence of milling operations.

NEW ELECTROSTATIC FIELD STRENGTH METER

A photograph of the electrostatic field strength meter mounted on a rubber mill is shown in Figure 1. It consists of three units: the modulator head, the audio amplifier, and the recording output meter.

MODULATOR HEAD

A photograph and line drawing of the modulator head are shown in Figures 2 and 3. This unit changes the electrostatic field into an alternating current voltage which is proportional to the field strength itself. This voltage, after amplification by the audio frequency amplifier, is rectified and recorded by the output meter.

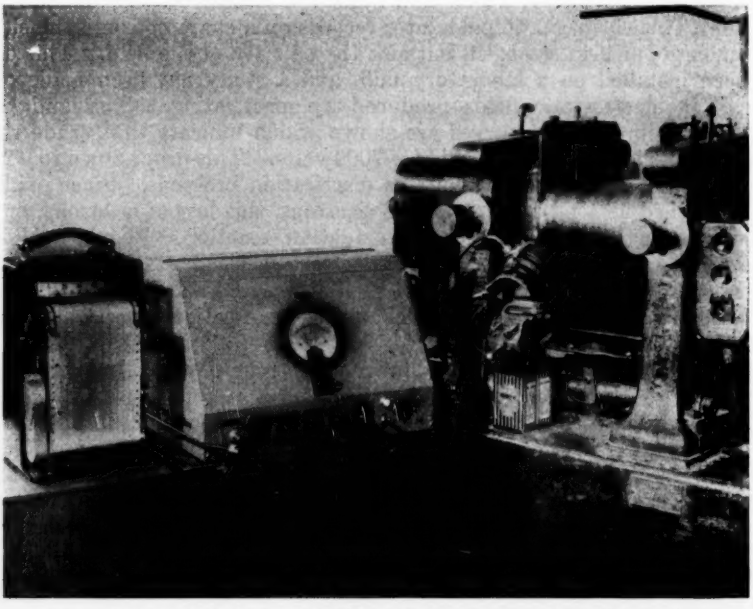

FIG. 1.—Photograph of electrostatic field strength meter mounted on rubber mill.

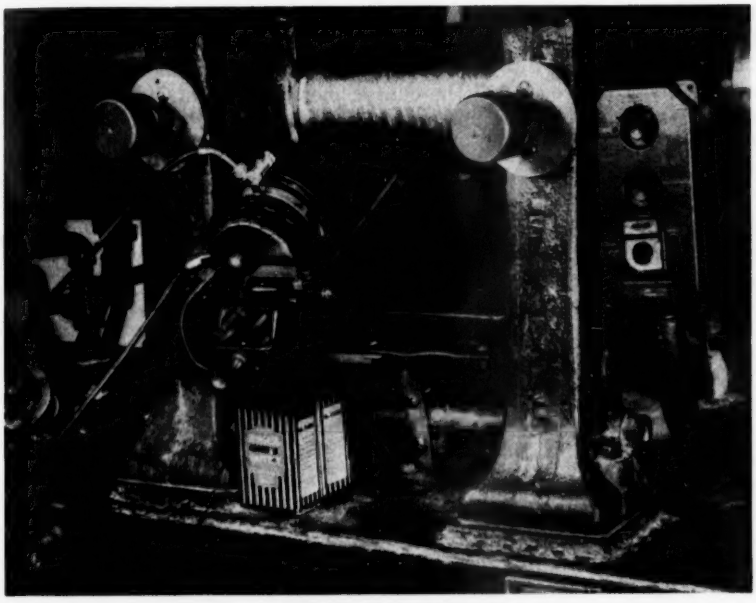

FIG. 2.—Photograph of modulator head.

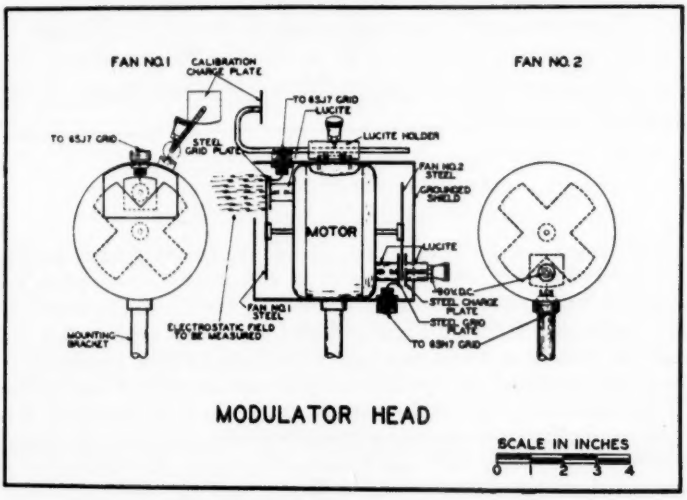

FIG. 3.—Line drawing of modulator head.

The operation of the No. 1 fan of the modulator (Figures 3 and 4) is similar to that described in our previous paper[2]. It cuts or modulates the electrostatic lines of force, or field, between the sample and the stationary plate connected to the grid of the audio frequency amplifier, thus producing the 3000-cycle audio frequency voltage. In the new unit, the specimen plate and lower charge plate of the old unit have been eliminated, for when they are continuously exposed to the electrostatic field they cause trouble by taking on a charge.

This modification of the old unit enabled the electrostatic field to be recorded continuously. However, it was observed that, on mastication of rubber, the charge curve started at a very high negative value, then dropped to zero; and as mastication proceeded, the charge increased again. This did not seem reasonable; and on checking polarity with a vacuum-tube voltmeter, the electrostatic field actually changed from negative (−) to positive (+) and, as expected, the rubber became less negative, or more positive, as mastication proceeded. This meant that, for the apparatus to be of value, it must distinguish polarity as well as measured magnitude of the electrostatic field.

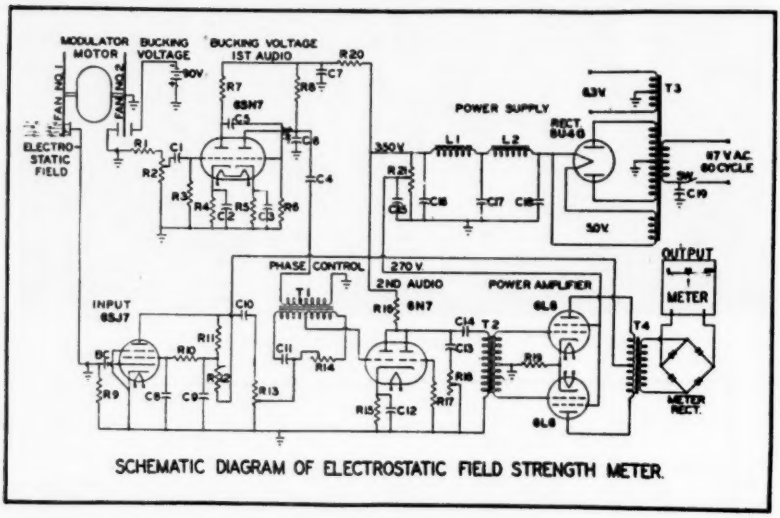

FIG. 4.—Schematic of audio amplifier.

POLARITY INDICATOR DEVELOPMENT

After considerable experimentation, it was observed that a positive electrostatic field produced a 180°-phase shift in the output wave when a cathode ray oscillograph was used as an output-meter. This led to the development of the second modulator fan (see Figures 3 and 4), which produced a voltage of fixed phase and the same frequency and wave form as that produced by No. 1 fan. These two voltages are applied in series to the grid of the second audio stage (6N7) (Figure 4). When they are in phase, they are additive; when 180° out of phase, as is the case when the polarity of the electrostatic field changes from negative to positive, they buck each other and the difference between them is recorded on the output meter. If they are of exactly the same magnitude when in phase, the reading is twice the value of either one; when 180° out of phase, the output meter is zero.

The magnitude of the bucking voltage from fan No. 2 (Figure 4) is adjusted by means of the volume control R_2 (Figure 4), so that the output meter reads center scale when the electrostatic field around fan No. 1 is zero. A phasing control also is provided (R_{14} in Figure 4), and it is adjusted so that reading on the output meter is zero when the alternating current voltages from fans Nos. 1 and 2 are equal and 180° out of phase. R_{18} is a secondary control to aid in

obtaining proper phase adjustments. Once adjusted, these controls seldom need to be readjusted. The gain control (R_{13}, Figure 4) is to adjust the sensitivity and range of the instrument. Six field-strength ranges, of 200 volts/in., full scale, to 10,000 volts/in., full scale, can be obtained conveniently by proper setting of this control.

AUDIO AMPLIFIER CIRCUIT

With the exception of the novel circuit for polarity indication, the audio amplifier circuit is similar to that used for public address work. The complete scheme is shown in Figure 4. It will be noted that the alternating current-voltage from modulator fan No. 1 is preamplified by a high-gain 6SJ7 voltage amplifier. The amplified voltage is then passed to the grid of the 6N7 second audio stage, then to the push-pull 6L6 beam power-output stage. It is then rectified by the selenium rectifier, and recorded on the recording output meter.

The so-called alternating-current bucking voltage from modulator fan No. 2 is produced from the 90 volt B battery supply source. It is amplified by the two-stage 6SN7 dual triode tube and passed on through the audio transformer and phase control circuit, and finally injected, in series with the amplified voltage from fan No. 1, into the grid circuit of the 6N7 second audio-amplifier tube. It then passes through the power-output stage to the recording output meter.

CALIBRATION OF FIELD STRENGTH METER

The instrument was calibrated by applying known high d.c. voltages (0 to 10,000 volts) to a large metal plate (36 × 36 inches) supported parallel to, and at various distances (1 to 5 inches) from, the modulator head. The field strength was found to vary linearly with the distance, so the meter was calibrated directly in field-strength units (volts per inch). The amplifier was designed to give a linear response; the calibration curve is shown in Figure 5.

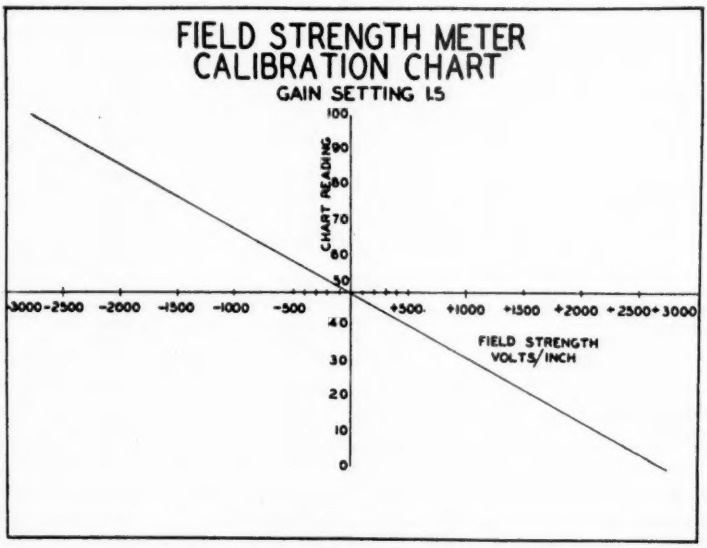

FIG. 5.—Field strength meter calibration chart.

Similar curves (all straight lines), which are not shown, were obtained for various gain control settings giving full scale ranges of 200 to 10,000 volts/in. If the modulator is 2.9 inches from the rubber, the actual voltages would be 2.9 times the field strength units shown in the calibration graph. For all the charts in this paper, the field strengths are reported in volts at 2.9 inches.

EXPERIMENTAL PROCEDURE AND RESULTS

The modulator head was mounted on a mill with a suitable bracket so that it could be moved toward or away from the rubber and also to the left or right. A distance of 2.9 inches from the rubber was found to be satisfactory. If the modulator is too close to the rubber (0.5 inch), there is danger of the electrostatic charge arcing over and discharging on the grounded shield, and also danger of damaging the modulator when cutting the rubber. If too far away, the field strength may be too low to operate the output recorder. The rod shown on the right side of the modulator touching the rubber is a guide with a miniature ball-bearing mounted in the end which rolls against the rubber. By means of this adjustable mounting, the modulator can be kept at a fixed distance away from the rubber as the rubber sheet becomes thinner from mastication. This rod can be dispensed with in all ordinary tests, since the change in charge due to change in this small distance is insignificant. The amplifier, modulator, and output system were check-calibrated before and

TABLE 1

COMPARISON OF ELECTROSTATIC FIELD STRENGTH AND MOONEY VISCOSITY OF VARIOUS POLYMERS MASTICATED ON A LABORATORY MILL

Polymer	Time of mastication (minutes)	Mooney viscosity (4 MS at 212° F)	Electrostatic field strength	
			Volts per inch	Volts at 2.9 inches
Rubber	0	57	−2240	−6500
Average for smoked sheet	5	29.5	−1100	−3200
and pale crepe	7.5	25	−475	−1350
	10	19	+345	+1000
GR-S-X180	0	27.5	−2340	−6760
Regular GR-S	5	26.5	−2070	−6000
	7.5	24	−1630	−4720
	10	23.5	−1390	−4020
GR-S 60	0	38.3	−1540	−4460
Cross-linked GR-S	5	33.5	−830	−2400
	7.5	31	−495	−1440
	10	28	−465	−1350
Philprene A	0	34.1	−515	−1500
41° F polymerizing	5	30.3	−138	−400
temperature	7.5	30.0	−138	−400
	10	29.7	−138	−400
GR-S-X435	0	34.5	−350	−1010
41° F polymerizing	5	29.9	−69	−200
temperature	7.5	29.3	−69	−200
	10	28.5	−69	−200
Philprene B	0	34.9	+450	+1300
14° F polymerizing	5	29.3	+480	+1400
temperature	7.5	28.7	+515	+1500
	10	28.0	+515	+1500

TABLE 2

MOONEY VISCOSITY OF VARIOUS POLYMERS

Polymer	Time of mastication (minutes)	Mooney viscosity—small rotor—212° F Minutes 0	1	2	3	4
Rubber	0	137	103	77	63.5	57
Average for crepe	5	43	33	32	30.5	29.5
and No. 1 smoked sheet	10	33	23	21	19.5	19
GR-S-X180	0	39	29.5	27.5	27	27.5
	5	33.5	20.1	28.7	27.6	26.5
	10	30.5	27.3	27	25	23.5
GR-S-60	0	42.5	43.2	42.5	40	38.3
	5	36	33	35.8	35	33.5
	10	33	29	30.5	28.5	28
Philprene-A	0	52.8	45	40	36.5	34.1
41° F	5	49.0	40.8	35.5	32.2	30.3
	10	42.1	38	33.9	31.2	29.7
GR-S-X435	0	49.5	39.7	32.4	36	34.5
U. S. Rubber	5	48.8	40	35.1	32	29.9
41° F	10	45.3	32.8	34	30.7	28.5
Philprene-B	0	51.0	45	40.8	37	34.9
14° F	5	46.0	39	34	31	29.3
	10	45.0	37	32	29.5	28

TABLE 3

COMPARISON OF ELECTROSTATIC CONTACT POTENTIAL[6] AND MOONEY VISCOSITY FOR VARIOUS POLYMERS MASTICATED ON A LABORATORY MILL*

Polymer	Time of mastication (minutes)	Mooney viscosity (4 MS at 212° F)	Electrostatic contact-potential in volts
Rubber	0	57	−3500
Average for No. 1 smoked sheet	5	29.5	−2500
and pale crepe	10	19	−1750
GR-S-X-180	0	27.5	−5300
	5	26.5	−4750
	10	23.5	−4500
GR-S-60	0	38.3	−4750
	5	33.5	−4250
	10	28	−4000

* Size of mill: 6 × 12 inches
Mill temperature: 130° F
Distance between mill rolls: 0.042 inch
Batch size: 300 grams

after each test by using a 45-volt B battery to furnish voltage to a one-inch plate held in the Lucite holder on top of the modulator (see Figure 3). This plate was set ¼ inch from the grid plate and output meter reading noted. After calibration, the plate was slid back out of place in the Lucite holder.

The bucking voltage control R_2 was first set so that the output meter would read half-scale when no charged object was near the modulator fan No. 1.

Three hundred grams of rubber was placed on the 6 × 12-inch mill, using a 0.042-inch distance between the rolls and 130° F mill-roll temperature. The

room temperature should be maintained essentially constant and the relative humidity constant and under 50 per cent to obtain duplicate results. The rubber was masticated, and the field strength around the rubber was recorded automatically on the output meter chart. Typical electrostatic breakdown curves, which are actual photographs of the Esterline Angus recorder charts, are shown for pale crepe, premasticated blend of No. 1 smoked sheet and pale crepe, regular GR-S X-180, cross-linked GR-S-60, Philprene-A (polymerized at 41° F), and Philprene-B (polymerized at 14° F) (see Figures 9 to 14). Table 1 lists average data for two or more sets. It will be noted that there is considerable difference in behavior between the various polymers in regard to both electrostatic field strength and Mooney viscosity.

MOONEY VISCOSITY

Mooney viscosity tests (see Tables 1, 2, and 3) were run with an NBS-model apparatus equipped with Brown electronic temperature and load recorders. The small rotor and a temperature of 212° F were used for all tests. Mooney values were reported for four-minute cycles, except in Table 2 where the Mooney values were reported for zero, one, two, three, and four-minute periods.

FIELD PATTERN

To determine the electrostatic field pattern around the rubber, the modulator was removed and held in six different positions while mastication proceeded. The results are shown in Figure 6 for a tight mill with relatively large bank, and for an open mill with small bank.

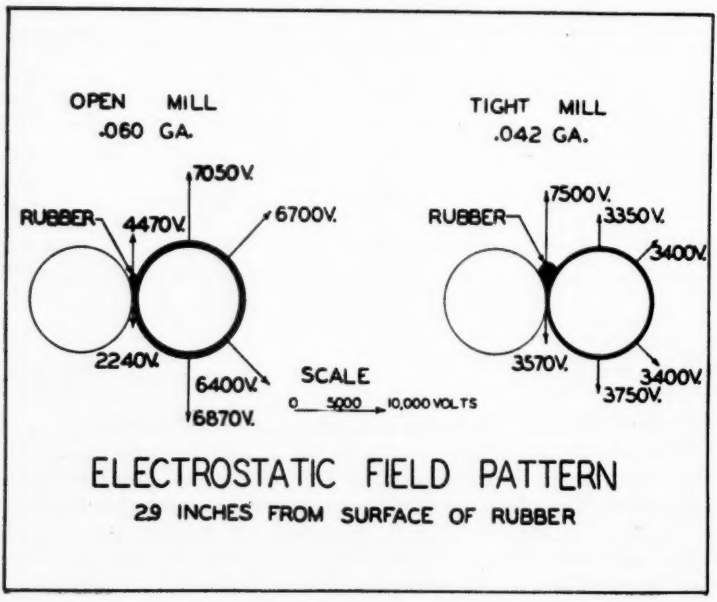

FIG. 6.—Electrostatic field pattern.

It will be noted that the strongest field is directly above the bank rubber on the tight mill, and the charge distribution becomes more uniform around the roll as the mill is opened wider. The high field strength at the bank possibly is due to the large area of the bank and its acting as a capacitor and storing up the charge.

ELECTROSTATIC CHARGE DISTRIBUTION

Charge-distribution tests are shown in Figure 7 and Figure 8 for rubber which has been masticated to the point where it shows the presence of a positive electrostatic field around it. By rolling the rubber inside in, as shown in Figure 7, the negative field, or charge, can be rolled up inside the rubber, and shows a positive charge. By rolling the rubber outside in (see Figure 8), the positive electrostatic field or charge can be rolled up inside the rubber; and it then shows a negative charge when brought near any electrostatic polarity charge-indicating device, such as a VTVM or our new modulator.

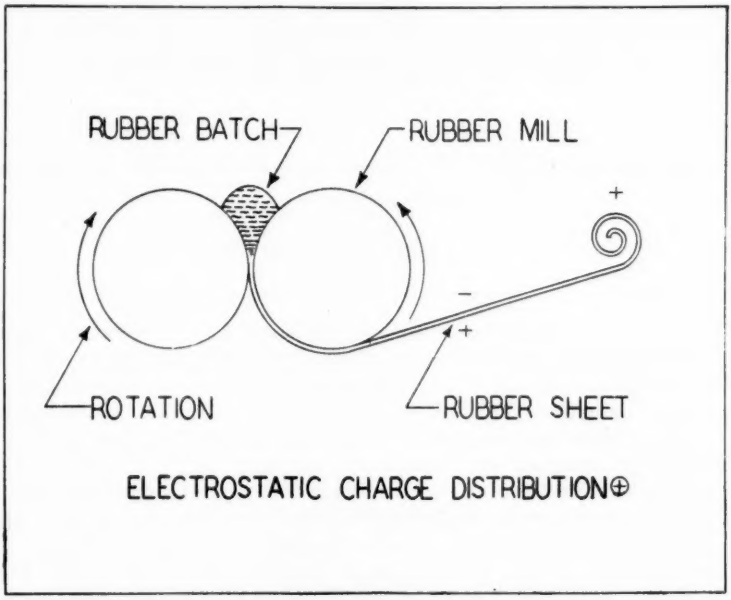

FIG. 7.—Electrostatic charge distribution (+) for (+) field.

ELECTROSTATIC CONTACT POTENTIALS

Electrostatic contact potentials were run, using the plunger apparatus described in a previous paper[2], for measuring cured rubber samples. The results in Table 3 indicate that, as the rubber is masticated, it becomes less negative. This checks the data obtained with the new modulator on electrostatic field strengths. However, all contact potentials are negative in charge; and there are no positive charges even on masticated rubber. This indicates that possibly the polar rubber on the mill was more highly oriented during mastication than when the steel plunger contacted the rubber in contact potential measurements.

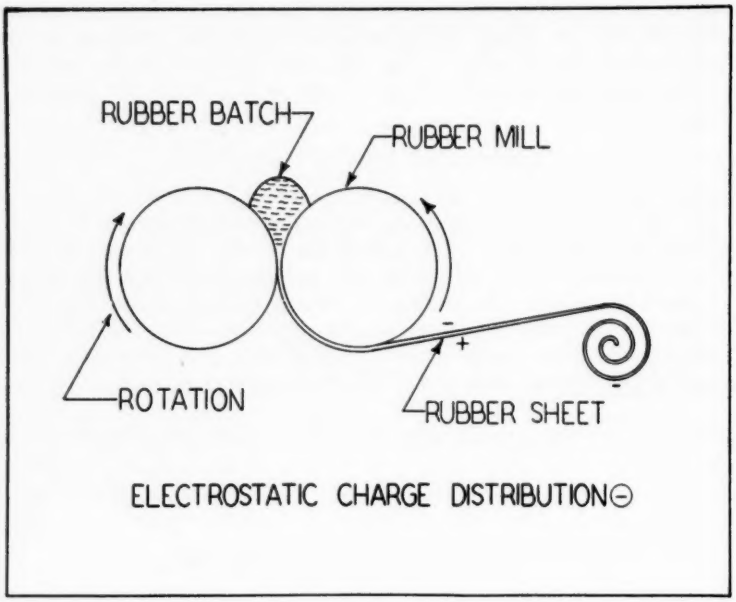

FIG. 8.—Electrostatic charge distribution (−) for (+) field.

DISCUSSION OF RESULTS

SOURCE OF ELECTROSTATIC FIELD

When any two dissimilar materials are brought into contact, electronic rearrangement takes place; hence when separated, one material becomes positive, the other negative. In other words, there is an interchange of electrons—what one gains, the other loses. All materials can be arranged in an electrostatic contact-potential series, and the particular place in the series depends on the composition of the material itself. For example, rubber and GR-S are on the negative end of the scale, whereas pigments like zinc oxide and carbon black are on the more positive (less negative) end of the scale.

In the mastication of rubber, the two dissimilar materials are the rubber and the steel mill-roll. When the rubber is squeezed into contact with the steel roll, electronic rearrangement takes place, and as the rubber rolls away from the roll, the rubber becomes negative and the steel roll becomes positive. This negative charge produces an electrostatic field around the rubber, which is measured with our modulator. The positive charge on the mill goes off to ground, since the mill is grounded. Any change in composition of the rubber due to mastication, oxidation etc., manifests itself as a change in field strength.

CAUSE OF POLARITY CHANGE

It is thought that, as rubber is masticated (Figures 9 and 10), oxygen reacts with the molecules, reducing the chain length and making it more polar[4]. Unoriented oxidized masticated rubber (Tables 1 and 3) has a less negative contact-potential than unoxidized unmasticated rubber; hence the electrostatic field strength becomes less negative with mastication. As mastication

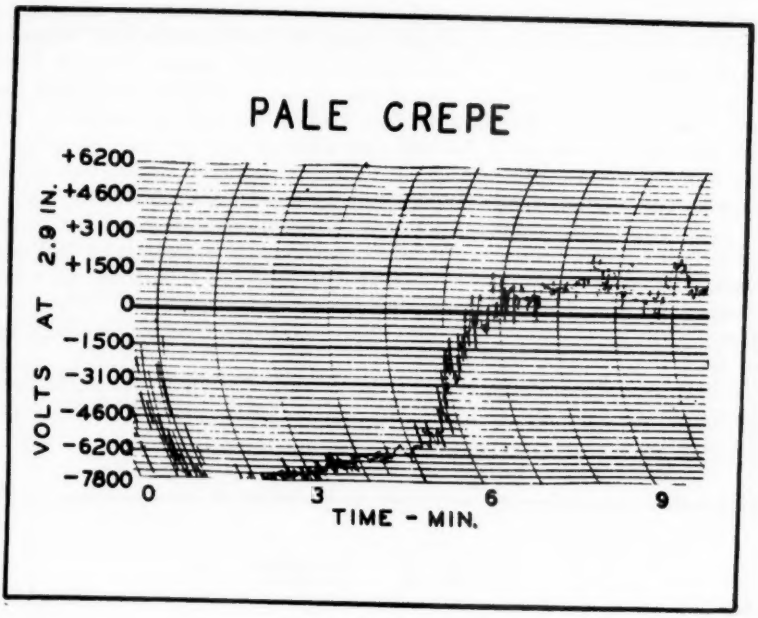

FIG. 9.—Crude crepe.

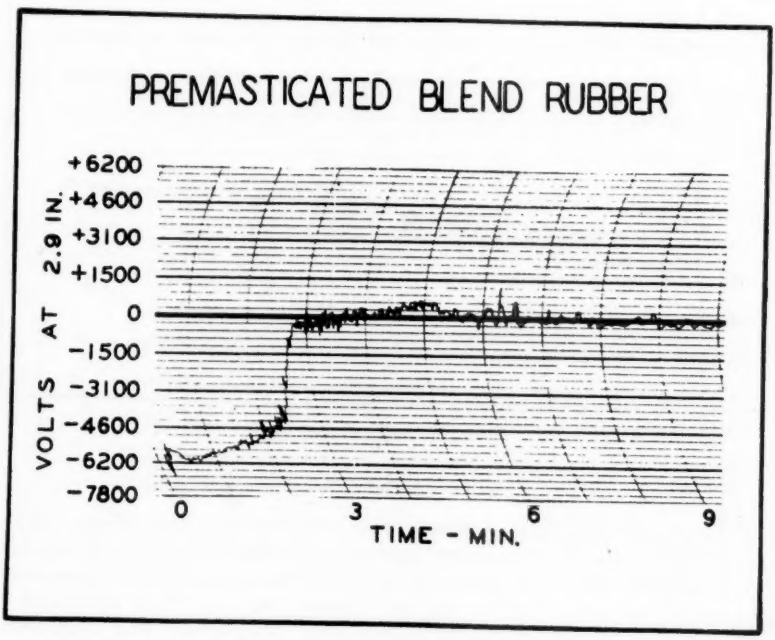

FIG. 10.—Premasticated blend rubber.

proceeds, more of the polar oxidized molecules become oriented or aligned until, finally, enough are aligned to produce a positive electrostatic field toward the end of the mastication cycle. This is indicated by the results shown in Figures 7 and 8, which indicate that one side of the rubber is positive, the other, negative, provided that the electrostatic field around the mill is positive. When positive rubber is taken from the mill and allowed to relax, the molecules assume a more random position and may become negative again (but never so negative as the original crude rubber). This is a further indication that the actual positive field is produced in part by alignment of the polar oxidized molecules. The polar nature of rubber is mentioned in an article by Williams[12]. The data on contact-potentials in Table 3 also bear out this, since the contact potentials were run without severe distortion of the rubber[2]. The loss in negative charge, in any case, indicates an oxidation reaction which supports the classic work of Cotton[6] and of Busse[7].

The results on cross-linked GR-S-60 (Figure 12) show some changes in electrostatic field strength and viscosity, as might be expected from a cross-linked material.

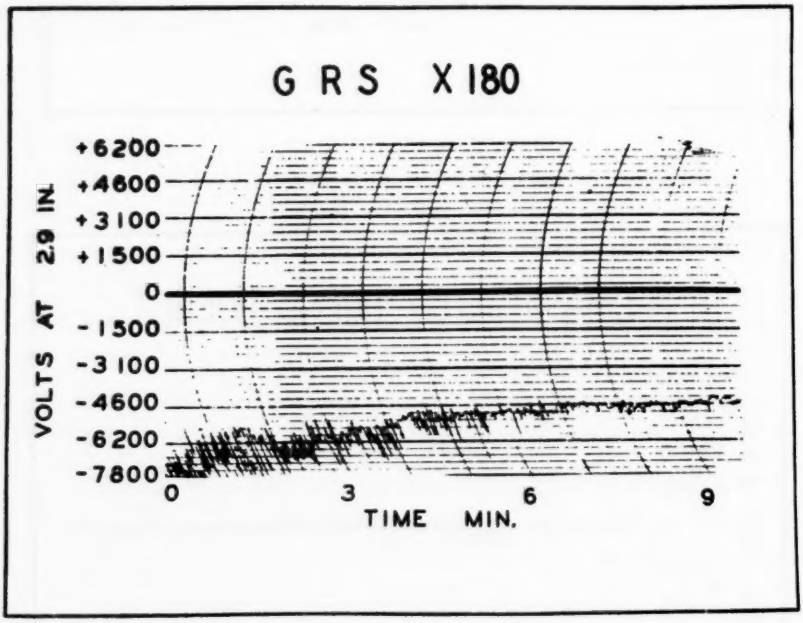

FIG. 11.—GR-S-X-180.

GR-S

Regular GR-S (122° F polymerization temperature) (see Figure 11) decreases in field strength to a limited extent on mastication, but does not break down like natural rubber, as indicated by both Mooney viscosity figures and by the shapes of the electrostatic curves. GR-S, because of its chemical and physical structure, is not so subject to oxidation, orientation, and alignment as is natural rubber; hence, gives a different electrostatic breakdown curve.

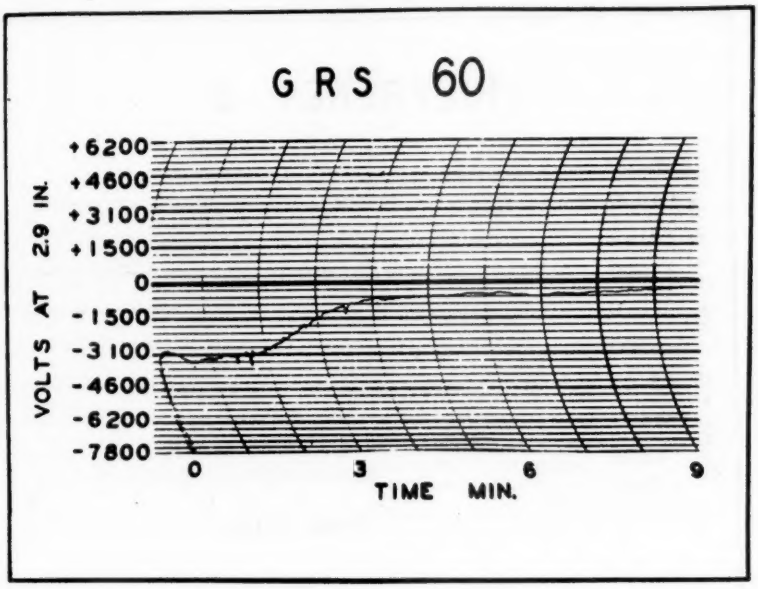

FIG. 12.—GR-S-60.

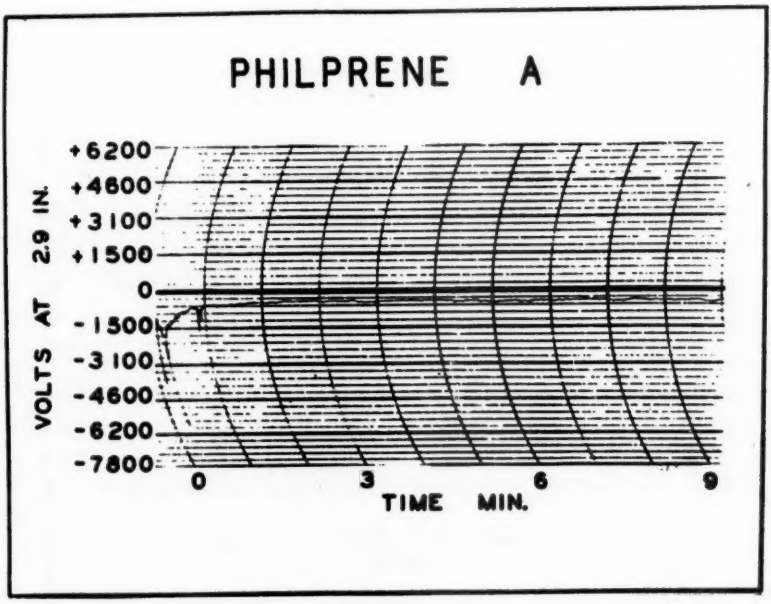

FIG. 13.—Philprene-A (41° F).

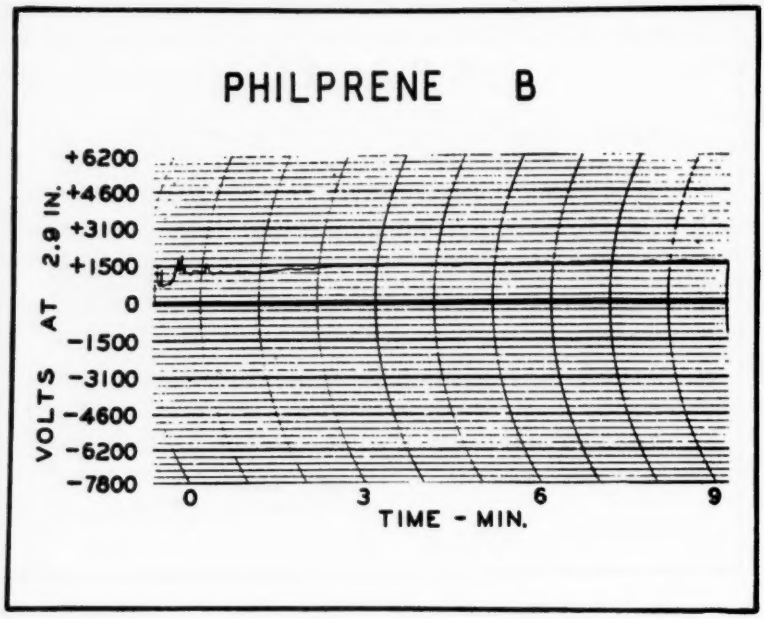

FIG. 14.—Philprene-B (14° F).

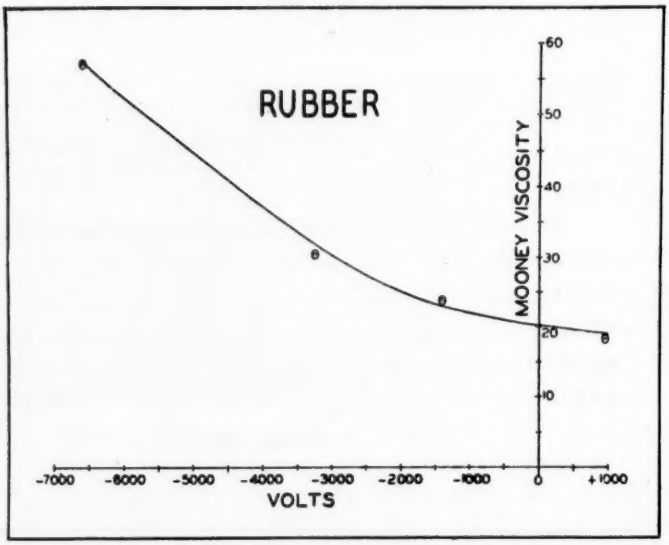

FIG. 15.—Electrostatic field strength *vs.* Mooney viscosity for rubber.

Philprene-A (41° F polymerization temperature) (see Figure 13) is unusual in that it gives an essentially zero electrostatic field throughout mastication. As the temperature of polymerization is lowered, the electrostatic-breakdown curves flatten and become less negative (see Figure 13); and in the case of Philprene-B (14° F polymerization temperature) (see Figure 14), the field actually is positive, which indicates unusual properties of this type of material in the crude state. Polymolecularity and unusual properties of this material in the crude state have been reported previously in an excellent paper by Shearon, McKenzie and Samuels[8] on the low-temperature manufacture of chemically made rubber.

The flat electrostatic breakdown curve indicates little or no breakdown during mastication of Philprene-B, and this is borne out by Mooney Viscosity tests. The positive and flat nature of the electrostatic curve, along with the other properties, indicates, also the presence of readily aligned, long-chain, somewhat polar molecules for this material.

In spite of the electrostatic breakdown curves for rubber and GR-S being widely different, there is nevertheless a partial correlation between plasticity and electrostatic charge, as shown in the Mooney viscosity *vs.* electrostatic charge curves of Figure 15 and Figure 16.

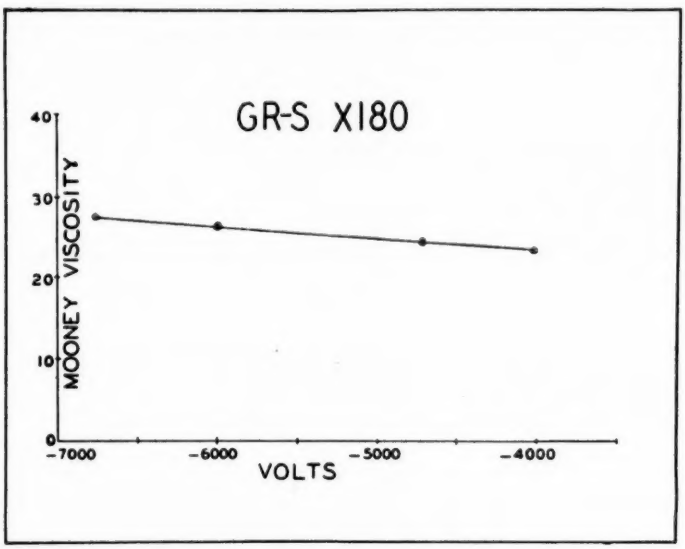

FIG. 16.—Electrostatic field strength *vs.* Mooney viscosity for GR-S.

SUMMARY AND CONCLUSIONS

A new electrostatic field strength meter has been described which measures and records, not only the magnitude of electrostatic fields, but also their polarity.

This device has been used in a study of the mastication of rubber, and has furnished data which indicate that rubber becomes less negative, and may actually become positive, as mastication proceeds; this indicates in turn an oxidation of the molecules as well as an electronic rearrangement and orientation of the rubber molecular chains.

Data on GR-S polymerized at different temperatures show entirely different electrostatic breakdown curves, which, with other physical characteristics, indicate unusual properties of the crude low-temperature polymers; *e.g.*, high molar weight, long-chain molecules, already or easily oriented, which do not oxidize or break up appreciably on mastication.

A partial correlation of Mooney viscosity and electrostatic contact-potential and field strength has been shown for rubber and GR-S which have been masticated on a rubber mill.

The new electrostatic-field strength meter shows promise as a new tool which can be used in processing control, and also as a research instrument for obtaining fundamental information on mastication, pigment dispersion and incorporation, as well as an aid in forming new concepts concerning the structure of matter.

ACKNOWLEDGMENT

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CONSTANTS FOR AUDIO AMPLIFIER

Shown in Figure 4

Transformers

T_1—Audio transformer UTC (0–7 Ouncer)
T_2—Interstage transformer
T_3—Power transformer
T_4—Output transformer—8-ohm secondary
Meter rectifier—selenium—10-volt, 250 MA
Putput meter—Esterline Angus recorder—100 MV, 250 MA, D.C. full-scale
B.C.—1-volt bias cell

Controls

R_2 —Bucking voltage gain control, 0.5-meg. potentiometer
R_{13}—Input gain control, 1-meg. potentiometer
R_{14}—Phase control, 0.5-meg. potentiometer
R_{15}—Tone control, secondary phase control, 100-K potentiometer

Condensers

C_1 C_4 C_5 C_8 C_{10} C_{19}	0.1 MF	C_{12}	25 MF
C_2 C_3	10 MF	C_{13}	0.05 MF
C_6	0.0015 MF	C_{14}	0.25 MF
C_7 C_9 C_{15}	8 MF	C_{16} C_{17} C_{18}	20 MF
C_{11}	0.005 MF		

Resistors

R_1 R_3	250 K	R_{11}	200 K
R_4	2.5 K	R_{12}	24 K
R_5	1 K	R_{15}	2250 ohms
R_6	0.5 Meg.	R_{16}	75 K
R_7 R_8	50 K	R_{17}	240 K
R_9	5 Meg.	R_{19}	300 ohms
R_{10}	1 Meg.	R_{20}	51 K

R_{21} 15-K voltage divider tapped at 10 K

REFERENCES

[1] Beach, *Elec. Eng.* **60**, 202 (1941); Cadwell, Handel, and Benson, *Ind. Eng. Chem. News. Ed.* **19**, 1139 (1941); Liska and Hanson, RUBBER CHEM. TECH. **15**, 678 (1942); Silbee, Natl. Bur. Standards. Circ. **C438** (June 10, 1942); Bulgin, *Trans. Inst. Rubber Ind.* **23**, No. 1 (1947).
[2] Havenhill, O'Brien, and Rankin, *J. Applied Physics* **15**, 371 (1944).
[3] Havenhill, O'Brien, and Rankin, *J. Applied Physics* **17**, 338 (1946).
[4] Busse, *Ind. Eng. Chem.* **24**, 140 (1932); Williams, RUBBER CHEM. TECH. **21**, 1 (1948); Dogadkin, RUBBER CHEM. TECH. **21**, 48 (1948).
[5] Williams, RUBBER CHEM. TECH. **21**, 1 (1948).
[6] Cotton, *Trans. Inst. Rubber Ind.* **6**, 487 (1931).
[7] Busse, *Ind. Eng. Chem.* **24**, 140 (1932).
[8] Shearon, McKenzie and Samuels, *Ind. Eng. Chem.* **40**, 774 (1948).

PHYSICAL PROPERTIES OF FRACTIONS OF GR-S AND THEIR VULCANIZATES*

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INTRODUCTION

This investigation, pertaining to the effect of number-average molecular weight on various physical and chemical properties of the vulcanizates of butadiene-styrene copolymers (75/25), designated as GR-S, and fractions thereof, was prompted by the obvious need of better bench marks by those engaged in producing and developing better synthetic rubbers.

By the use of modifiers, or chain terminators, it has been possible to produce GR-S samples, gel-free, with varying viscosity average molecular-weight values, as indicated by appropriate viscosity measurements. Qualitatively, those samples having the higher intrinsic viscosity values, when compounded in a Santocure tread-type recipe, gave vulcanizates with better physical properties. However, it was felt that additional and more detailed data were required to show the effect of molecular weight on the physical properties of vulcanized GR-S, assuming that only minor changes are encountered in chemical structure. Attempts to answer this problem could be made in two ways: the first method involves the determination of the effect of varying molecular-weight distributions on the desired cured physical properties; the second method is to determine the physical properties of the vulcanizates of the fractions of the GR-S sample. The latter method was employed in this investigation.

When vulcanized, the GR-S molecules are cross-linked into a network structure by small percentages of sulfur. This vulcanized structure can be characterized by an average molecular weight, and(or) the molecular-weight distribution between points of cross-linking. Basically, it can be said that the resultant vulcanized structure of GR-S is a function of the average molecular weight (or molecular-weight distribution of a heterogeneous sample) just before vulcanization and the proportion of effective cross-linking agent employed. It is evident that the average molecular weight of molecular-weight distribution of GR-S just before vulcanization is not equivalent to these parameters as determined on the unmilled uncompounded GR-S, since the compounding processes employed by the rubber industry bring about changes in the sol–gel characteristics of GR-S, such as a reduction in the magnitude of the molecular weights of the benzene-soluble units and a reduction in the amount and change of structure of gel material present. These changes occur during milling and processing cycles.

An excellent study on the effect of molecular structure on the physical properties of Butyl rubber has been made by Flory[1]. The present study on

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GR-S was complicated by the fact that GR-S, unlike Butyl rubber, has a structure which is believed to deviate considerably from linearity; and when compounded it undergoes measurable mechanical breakdown, oxidative breakdown and, under high-temperature conditions, it often undergoes gelation. However, it was felt that by employing a standard milling procedure and by characterizing the unfractionated GR-S and GR-S fractions before milling and also before the addition of carbon black useful information could be obtained concerning the effect of the number average molecular weights of unmilled and milled fractions on the resultant physical properties of the vulcanizates of these samples.

Other variables, such as percentage of styrene, rate cold-mill breakdown, percentage shrinkage of uncompounded and compounded stocks, and Mooney plasticity values, were studied as a function of number average molecular weight.

EXPERIMENTAL METHODS

Fractionation.—Fifteen hundred grams of GR-S (sample X-55) was cut into thin pieces and placed in a 12-gallon Pyrex vessel containing 34 liters of C.P. acetone. After 3 days, during which time the solution was kept in darkness and stirred intermittently, the acetone solution was removed. Then the copolymer was similarly extracted with 34 liters of methanol, and the methanol solution obtained was combined with the acetone solution. This solution was concentrated at room temperature in darkness and was then placed in a vacuum oven where the solvents were completely removed after 3 days at 30° C at reduced pressure. This lowest molecular fraction contained 127 grams of material, consisting of free soap, fat acid, age-resistor, and low-molecular copolymer. The remaining extracted GR-S sample was redissolved in 35 liters of C.P. benzene containing 1 per cent antioxidant (phenyl-β-naphthylamine) on the copolymer.

Isolation of the narrowed molecular fractions of GR-S was carried out by a fractional precipitation technique similar to that employed by Flory[2], with benzene as the solvent and methanol as the precipitant. To the GR-S solution, thermostatted at 30° C in a large air bath, methanol was added slowly and the solution was stirred until the desired amount of precipitation had occurred; the solution was then warmed until the precipitated phase had redissolved. Reprecipitation was allowed to occur by slowly cooling the solution to 30° with moderate stirring. The solution was then allowed to stand in the dark for 2–3 days at 30°; during this time the higher molecular units precipitated completely. After the precipitated phase (approximately 200–250 grams of copolymer) was carefully isolated, it was redissolved in approximately 30 liters of C.P. benzene and reprecipitated as mentioned before to give Fraction 1. The amount of methanol added was regulated so as to obtain approximately 150–200 grams of copolymer in the final fraction. To the precipitated phase containing Fraction 1 was added 1 per cent of phenyl-β-naphthylamine on the fraction and 2 liters of benzene; aliquot portions of this solution were then coagulated with excess methanol to obtain sufficient amounts of Fraction 1, which was then dried under reduced pressure at 25°. For osmotic pressure work, these aliquots were coagulated by a large excess of methanol to reduce the phenyl-β-naphthylamine content to a minimum. The soluble phase obtained on the first precipitations was combined with the soluble phase obtained in the reprecipitation step of Fraction 1, and these were allowed to concentrate at room temperature in darkness in the presence of phenyl-β-naphthylamine.

After concentrating to a suitable volume, the precipitation process was repeated to obtain Fraction 2, and subsequent fractions. To obtain good separations, the first precipitation of a given fraction took place in a polymer solution whose concentration varied from 0.8 to 2.5 per cent, and the second or later precipitations took place in 0.3 per cent solutions. Fractions 1–6 were precipitated at least twice from dilute polymer solutions whose concentrations were approximately 0.3 per cent.

Sol–gel measurements.—GR-S and other copolymers made from diolefin monomers often contain some gel material that is thought to be present as a consequence of branching and cross-linking in the copolymer. Characterizations of the gel and sol material present in the GR-S fractions and in the unfractionated GR-S were made in terms of percentage of gel content, swelling index of the gel portion, and the intrinsic viscosity of the benzene-soluble portions.

Essentially, the sol–gel separations were carried out as recommended by the *Office of Rubber Reserve Committee on Standardization of Methods and Apparatus for Determining Molecular Weights of Polymers*, with a few minor changes. This procedure involved the placement of 0.3000 ± 0.0002 gram of copolymer cut into fine pieces on a screen rack ensemble consisting of five 50-mesh circular screens mounted on a stainless tube—each screen being approximately 40 mm. in diameter and 12 mm. apart. This screen rack unit was then placed in a flat-top Pyrex weighing bottle, 45/12 T.S., 40×80 mm., containing 75 cc. of C.P. benzene. The standard taper weighing bottle was capped and, after 72 hours at room temperature, the benzene-soluble portion was removed and filtered through Grade-C sintered glass filters. The determination of the amount of soluble material present in a 25-cc. aliquot enables one to calculate the percentage gel content.

The ratio of the swollen gel weight to dry gel weight gives a number, defined as the swelling index of the gel portion, that essentially characterizes the tightness of the gel structure, and, in some measure, the average molecular weight between points of cross linking in the gel structure.

Intrinsic viscosity measurements.—Viscosity determinations were made in calibrated Ostwald viscometers employing 5 cc. of polymer solution. The kinetic energy correction factors of the viscometers employed were 1.5 per cent or lower. All viscosity work was performed at $25.00° \pm 0.01°$ C, with C.P. benzene as a solvent. After temperature equilibrium had been attained, the times of flow were timed to the nearest 0.1 second, and at least 3 determinations were made on a given concentration with a reproducibility of ± 0.15 second. Viscosity measurements were made in this fashion on three or more concentrations of a given polymer solution, and the intrinsic viscosities were calculated from the expression:

$$[\eta] = \frac{\ln (t/t_0)}{c}$$

where $[\eta]$ is intrinsic viscosity, t is time of flow of polymer solution in seconds, t_0 is time of flow of pure solvent in seconds, and c is concentration of polymer solution in grams of polymer per 100 cc. of solution at 25.00° C.

Viscometers were cleaned after each run with benzene, nitric acid, distilled water, and redistilled acetone, and were dried before running the next viscosity measurement.

Limiting intrinsic viscosities, $[\eta]_0$, were obtained from the plot of $[\eta]$ *vs.* concentration extrapolated to zero concentration.

Osmotic pressure measurements.—All the osmotic pressure work was performed with newly designed precision stainless-steel osmometers, which will be described in a later report.

A large amount of experimental work was performed evaluating semipermeable membranes prepared from the following materials and treated in various ways: cellophane, collodion, porous stainless steel metal impregnated with $Cu_2Fe(CN)_6$ or with collodion or collodion plus $Cu_2Fe(CN)_6$, and undried regenerated cellulose film.

The best semipermeable membranes were prepared from undried cellulose film, Type 330, obtained from Sylvania Industrial Corporation, Fredericksburg, Virginia, and were treated in the following manner. The film was immersed in 10 per cent NaOH solution at room temperature for 30 minutes and then immersed for 2–4 minutes in distilled water and for 10 minutes in the following solvents in the order indicated: acetone, ethyl alcohol, ethyl alcohol/benzene (50/50), and benzene.

Osmotic pressure measurements were made at 25.000° ± 0.005° C on the benzene-soluble portions of the GR-S fractions and unfractionated GR-S, using a combination of the static and dynamic methods. A Gaertner cathetometer, reading directly to 0.005 cm., was used to measure the osmotic pressure values. Equilibrium was approached from both sides, employing different osmometers; rechecks on each solution indicated a reproducibility of approximately 5 per cent for Fractions 2–7. Matched precision bore capillary tubing was employed in the osmometers, and it was found thot no corrections for surface tension of the polymer solutions were required over the concentration ranges employed.

In general, equilibrium values were obtained in approximately 50 hours at 25° C with the membranes employed, and, after the completion of each run, the solvent side of the osmometer was checked for dialyzed material by a total solids determination on the entire quantity of solvent employed. In all cases, with the exception of Fractions 8 and 9, less than 1–2 per cent of solute had diffused through.

Data typical of an experimental run are plotted in Figure 1. Fraction 8 contained 8 per cent of material which diffused through in 50 hours; Fraction 9

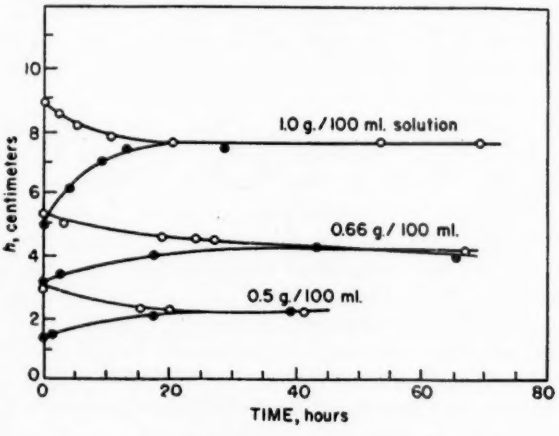

FIG. 1.—Osmotic pressure versus time, using Fraction 4.

was definitely too permeable for the membranes employed to give reliable osmotic pressure values.

The equilibrium osmotic pressure values of three or more concentrations of the solutions of polymer or fractions were determined and the plot of h/c *vs.* c was extrapolated to zero concentration to give the limiting osmotic pressure values. Osmotic pressure rise (h) was expressed in centimeters of benzene at 25.00° C, and the concentration term (c) in grams of solute per 100 cc. of solution at 25.00° C.

Osmotic pressure determinations were also made on the unfractionated GR-S sample, which had its low molecular material removed by slowly dropping a benzene solution of GR-S into a beaker containing a large excess of methanol. The precipitated material was extracted for 2 hours, then redissolved in benzene, and precipitated by methanol as before. The precipitated material was vacuum dried at 25° C, and then redissolved in C.P. benzene for osmotic pressure work.

Compounding.—All the fractions and the unfractionated GR-S were compounded in a Santocure tread-type recipe as follows:

Copolymer	100 parts by weight	Copolymer	100 parts by weight
Carbon black (E.P.C.)	50.0	Stearic acid	1.5
Zinc oxide	5.0	Santocure	1.2
Paraflux	5.0	Sulfur	Variable

Fifty-eight grams of copolymer was milled for 3 minutes on a 4 × 9-inch mill, with the mill rolls at approximately 20° C, and with a clearance of approximately 0.01 inch. The compounding ingredients were then added in the order: zinc oxide plus Santocure, carbon black, stearic acid plus Paraflux, with respective milling times of approximately 3, 15, and 5 minutes. During this time, the batch was cut back and forth repeatedly for thorough blending. Sulfur was then added to the batch, and the stock was rolled up and passed endwise through the mill 6 times. It was then set aside for 24 hours, then remilled for 3 minutes before samples were prepared for curing. Semimicrotesting techniques were employed in procuring stress–strain flexing and hysteresis data as described by Juve and Schroeder[3], and Shearer[4]. Durometer hardness, percentage Schopper rebound, percentage initial compression, and permanent set values were also obtained on the cured stocks. Quality index values were calculated by the method suggested by Juve[5].

Percentage of bound styrene.—Fractions 1–9 and a sample of the unfractionated GR-S samples were each suspended in C.P. benzene for 24 hours, and each sample was then coagulated with excess methanol. The coagulated samples were allowed to remain in excess methanol for 24 hours, removed, redissolved in benzene, and recoagulated with excess methanol. Due to the presence of a large amount of fat acid and free soap in Fraction 9, this fraction was extracted for 24 hours with distilled water at 50° C before the above methyl alcohol purification process. The samples were dried at 60° C in an air-circulating oven for 8 hours and then refractive index measurements were made as outlined by Madorsky and Wood[6] on Fractions 1–6 and on the GR-S sample. Due to the low molecular weights of Fractions 7, 8, and 9, refractive index measurements were made by the usual method employed for liquids.

CHARACTERIZATION OF FRACTIONS AND UNFRACTIONATED GR-S

Sol–gel properties.—Sol–gel properties of the large-scale GR-S fractions and the unfractionated GR-S sample were determined on samples protected with 1 per cent of phenyl-β-naphthylamine as the antioxidant, and which had been dried under reduced pressure in the dark at 25° C. The data are listed in Table I.

TABLE I

SOL–GEL PROPERTIES AND PHYSICAL APPEARANCE OF GR-S FRACTIONS

Fraction	Percentage gel	Swelling index	$[\eta]_0$	Physical appearance
1	83	261	6.57	An extremely tough rubber resembling vulcanized rubber. Excellent films.
2	69	137	3.85	Similar to Fraction 1 (but not as tough), and short.
3	0	—	2.86	Not as tough or as short as Fraction 2. When elongated, some fine, dry threads or legs appeared.
4	3	—	1.68	A much softer rubber than Fraction 3. It was too soft to have appreciable elongation, and the rubber, when pulled apart, yielded many fine, dry legs, which disintegrated into a powder. In texture this fraction resembled a processed cheese.
5	0	—	1.07	A softer rubber than Fraction 4. It was not sticky at room temperature and was too soft to have appreciable elongation. When the rubber was pulled apart, it yielded a few dry legs which were described for Fraction 4.
6	0	—	0.90	A softer rubber than Fraction 5. At room temperature, it was slightly sticky and at 30–33° C it was very sticky.
7	0	—	0.54	Much softer than Fraction 6. It was very sticky at room temperature.
8	0	—	0.30	Much softer than Fraction 7. It was very sticky, and was similar to molasses with respect to viscosity. At 30° C, it flowed like a heavy oil.
9	0	—	0.08	At 20° C, the sample did not appear to be so fluid as Fraction 8; this was due to the large amount of fat acid in this fraction. However, on warming to 35–40° C, this sample was less viscous than Fraction 8.

The sol–gel data indicate that the higher molecular fractions, obtained from the initially totally soluble butadiene-styrene copolymer, undergo considerable gelation, even when dried at reasonably low temperatures in the presence of an antioxidant.

In view of the interest in high molecular copolymers, these data are interesting, for they indicate the ease of gelation or cross-linking of high molecular copolymer chains. It is to be logically expected that these high molecular units would be more sensitive to the higher temperature processing conditions normally employed in the rubber industry.

On the other hand, the lower molecular fractions are comparatively unchanged by high temperature and milling effects in that little changes are incurred under these conditions in sol–gel properties (which we have found to be the most sensitive measurement of structural changes in copolymers).

Since a network structure essentially can be characterized by the average molecular weight (molecular-weight distribution) between points of cross-

linking, it is to be expected that these high molecular fractions would have sol–gel and swelling index relationships different from those encountered in unfractionated rubber. The experimental data show that the higher the molecular weight of a fraction (as indicated by the $[\eta]_0$ of the benzene-soluble portions) the greater the gel content of the dried fraction. For the given percentages of gel contents of Fractions 1 and 2, unusually high swelling indices were obtained, indicating that the average distance or average molecular weight between points of effective cross-linking in the three-dimensional gel structure was greater than that normally encountered in the past in unfractionated butadiene-styrene copolymers of similar gel contents.

Nine fractions of GR-S were obtained, each comprising approximately 11 per cent by weight of the original copolymer, which ranged in appearance from a very tough rubber to a liquid at approximately room temperature. Table I describes the physical characteristics of these fractions.

Limiting intrinsic viscosities.—Solutions of high polymers, particularly the high-molecular fractions, which are somewhat homogeneous with respect to molecular weight, characteristically behave in a nonideal manner. Accordingly, to obtain the most reliable data, one finds that various measurements made on these high polymer solutions, such as osmotic pressure and intrinsic viscosities, must be corrected for the concentration effect by suitable extrapolations to zero concentration.

A plot of intrinsic viscosity, as calculated from the expression $\frac{\ln (t/t_0)}{c}$ *vs.* concentration, is made in Figure 2; the resultant limiting intrinsic viscosity values are also indicated. These values decrease from Fraction 1 through Fraction 9, indicating that the fractionation procedure employed was effective in separating fractions on the basis of molecular weight differences.

Over the concentration ranges studied, the data indicate in general that the intrinsic viscosity values vary as a straight line function of the concentration terms for the fractions examined. However, the negative slope of the straight line plot of $\ln \frac{(t/t_0)}{c}$ *vs.* concentration increases as the molecular weight of the fraction increases, demonstrating the greater dependence of the $[\eta]$ values of the higher molecular fractions on the concentration variable. The $[\eta]$ values of the lower molecular fractions are not affected measurably by a reasonably large change in concentration.

Number-average molecular weights.—By using the new precision osmometers and the undried regenerated cellulose film (treated with NaOH–acetone) as semipermeable membranes, the osmotic pressure equilibrium values were obtained at 25.000° ± 0.0005° C for 3 different concentrations of a given polymer solution. Equilibrium values measured as centimeters of benzene at 25.00° C were usually obtained in 50 hours, and were approached from both sides, as indicated in Figure 1.

The number-average molecular weights ($\bar{M}_n$) were calculated by the familiar equation of van't Hoff which is expressed for ideal solutions as:

$$M = \frac{RT}{(\pi/c)_{c \to 0}}$$

where M is molecular weight, R is gas content, T is absolute temperature employed, π is osmotic pressure in atmospheres[7], and c is concentration of solution in grams per 100 cc. of solution.

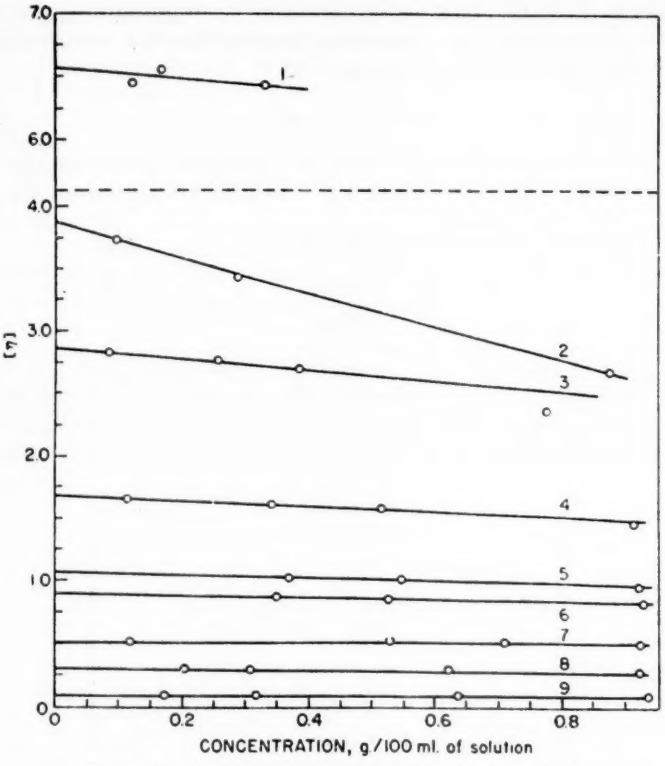

FIG. 2.—Intrinsic viscosities *vs.* concentration of GR-S fractions.

The above equation can be simplified to give the following equation when benzene at 25.00° C was employed as the solvent:

$$M = K/A$$

where $A = (h/c)_{c \to 0}$ and $K = 2.89 \times 10^5$. For each fraction studied, a plot of h/c versus c gave essentially straight lines over the concentration range examined. By extrapolation to zero concentration, the limiting osmotic pressure values were obtained and, using these values, the number-average molecular weight was calculated as shown in Table II.

TABLE II

NUMBER-AVERAGE MOLECULAR WEIGHTS OF GR-S FRACTIONS

Fraction	$[\eta]_0$	$(h/c)_{c \to 0}$	$\overline{M}_n$	μ_1	Weight (g.)	Weight (%)
1	6.57	0.175	1,652,000	0.454	210.72	14.1
2	3.85	0.40	723,900	0.348	214.67	14.3
3	2.86	0.60	482,000	0.348	180.76	12.0
4	1.68	1.5	193,000	0.336	150.50	10.0
5	1.07	2.8	103,400	0.306	166.90	11.2
6	0.90	4.4	65,800	0.352	157.80	10.5
7	0.54	12.25	23,600	0.377	119.00	7.9
8	0.30	23.375	12,400	0.358	172.25	11.5
9	0.08	—	—	—	127.40	8.5
X-55	2.36	3.0	96,500	0.394	—	—

It is evident from the data in Figure 3 that the reduced osmotic pressure values increase markedly with concentration and that this relationship may be conveniently represented by the equation:

$$\pi/c = A + Bc$$

where the intercept on the y axis is given by A and the slope of the line by B. This linear relationship between π/c and c has been deduced on theoretical grounds by Flory[8] and Huggins[9].

Huggins' equation is expressed as follows:

$$\frac{\pi}{c} = \frac{RT}{M} + \frac{RTd_1}{M_1 d_2^2}(\tfrac{1}{2} - \mu_1)c$$

where π is the osmotic pressure in atmospheres, c the concentration of solute in grams per cc. of solution, d_1 the density of solvent, M_1 the molecular weight of solvent, d_2 the density of solute, and μ_1 a constant which gives an approximate characterization of a given solute–solvent system at a given temperature.

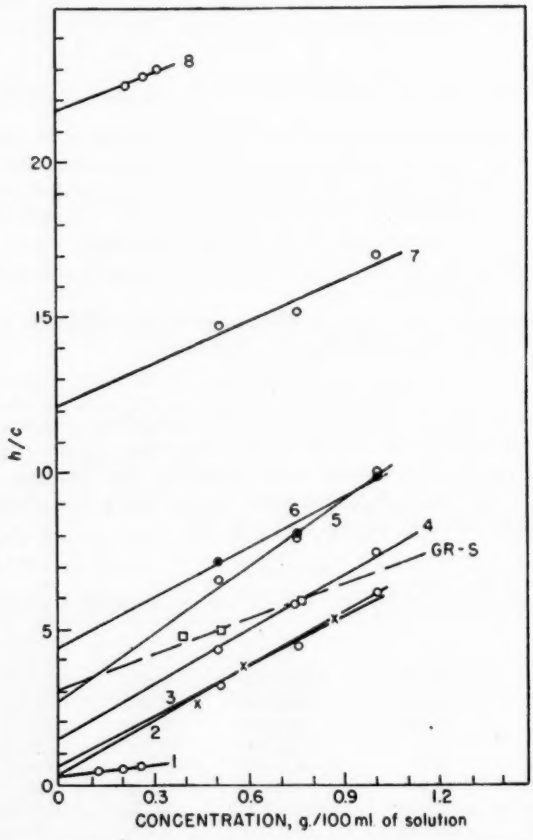

FIG. 3.—Reduced osmotic pressure *vs.* concentration of GR-S fractions.

By use of the above equation, the μ_1 values were calculated from the slopes of the reduced osmotic pressure plots presented in Figure 3, and were found to be essentially independent of molecular weight through the range 12,400 to 724,000. For Fractions 2–8 the values were found to be approximately 0.35; however, a slightly larger μ_1 value was obtained for the highest molecular fraction which had a number average molecular weight of 1,650,000. In view of the styrene content of each fraction (discussed elsewhere in this paper) there is not sufficient evidence to attribute the differences found in μ_1 values to structural changes.

Osmotic pressure measurements on the highest molecular fraction were made with difficulty, and the data obtained on this fraction were subject to the largest percentage errors.

It is evident from the number-average molecular weight values listed for each fraction in Table II that a large molecular-weight range was covered, as represented by nine fractions. For this reason there is still some molecular weight heterogeneity in these fractions, particularly those on the high molecular-weight end. The relationships between weight, intrinsic viscosity, and number-average molecular weights are given, respectively, by the expressions described by Flory[1]:

$$\bar{M}_w = \sum_i N_i M_i^2 / \sum_i N_i M_i$$

$$\bar{M}_v = [\sum_i N_i M_i^{a+1} / \sum_i N_i M_i]^{1/a}$$

$$\bar{M}_n = \sum_i N_i M_i / \sum_i N_i$$

where N_i is the number of molecules of molecular weight M_i and a is the exponent in the equation $[\eta] = K\bar{M}_v^a$.

By use of a log-log plot of the $[\eta]_0$ values of each fraction *vs.* the corresponding number-average molecular weight, a linear plot was obtained through the molecular weight range from 12,400 to 1,650,000. Then, employing the method of least squares for the most reliable osmotic pressure values (Fractions 2–7), the best straight line was determined for these points to be represented by the equation:

$$\log M = 4.95 + 1.51 \log [\eta]_0$$

or:

$$[\eta]_0 = KM^a$$

where $K = 5.4 \times 10^{-4}$ and $a = 0.66$. The above equation represents a very close check on the equation recently published by French and Ewart for GR-S fractions[10].

EFFECT OF $\bar{M}_n$ ON PHYSICAL PROPERTIES OF GR-S FRACTIONS

The most interesting problem was to determine the effect of the number average molecular weight of the unmilled fractions on the compounded physical properties of the fractions of GR-S.

By the use of the Santocure tread-type recipe previously described, 58 grams of each fraction (1–7) were compounded on a cold 4 × 9-inch mill. Fractions 8 and 9 were too liquid in nature to be compounded in the normal fashion on the mill, and were therefore compounded by the use of a hand homogenizer. Employing benzene as the dispersion medium, stearic acid, carbon black, zinc oxide, Santocure, and sulfur (in the order named) were dispersed in benzene, using the homogenizer. To this benzene dispersion of

compounding ingredients was added a benzene solution of the given fraction, and the resultant mixture was passed through the homogenizer many times. Benzene was permitted to evaporate at room temperature and the residual solvent was removed at reduced pressure at 25° C. When the fraction was free from solvent, it was mixed on a cold mill for ten minutes and removed. Evidence was obtained which indicated that excellent dispersions of carbon black were obtained for Fractions 8 and 9.

Preliminary testing was performed, covering three different sulfur ratios and five curing times at 280° F for each sulfur ratio employed, so as to determine the optimum curing time and sulfur ratio for each fraction. Optimum sulfur ratio was arbitrarily defined as that percentage of sulfur which would give a properly cured stock having a 300 per cent modulus value of 1000 lbs. per sq. in. This was done in this manner so as to obtain valid comparisons of the flex-life ratings of each of the fractions. Stress–strain data were obtained on a Scott machine for each sulfur ratio and curing time studied at every 100 per cent increment of elongation, using the automatic spark recorder described by Shearer[4].

The effect of varying curing times on the stress–strain data obtained for a given sulfur ratio on Fraction 1 is demonstrated in Figure 4. Similar data were obtained for Fractions 2–6.

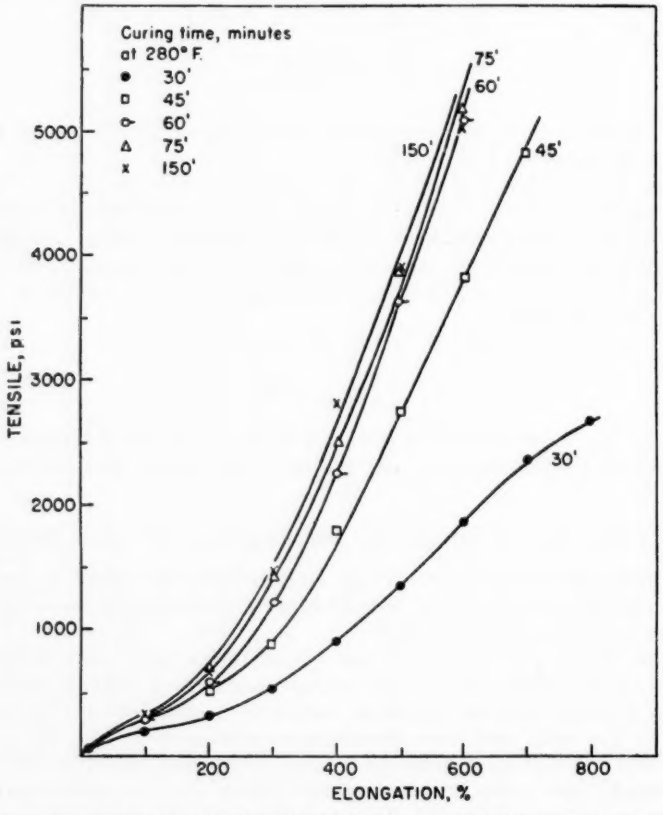

FIG. 4.—Stress–strain properties of Fraction 1 cured with 1.75 parts of sulfur per 100 parts of rubber.

The stress-strain data at break and the 300 per cent modulus values are listed in Table III. Corresponding plots of these physical properties of Fractions 1–7 *vs.* curing time indicated that curing for 75 minutes gave optimum physical properties for a given sulfur ratio.

When 1.75 parts sulfur per hundred parts of rubber (PHR) was used, only Fractions 1–6 were vulcanizable; and only these fractions contributed measurably to the physical properties of the vulcanized, unfractionated GR-S cured in a standard recipe employing 1.75 parts of sulfur. Fraction 7 had a

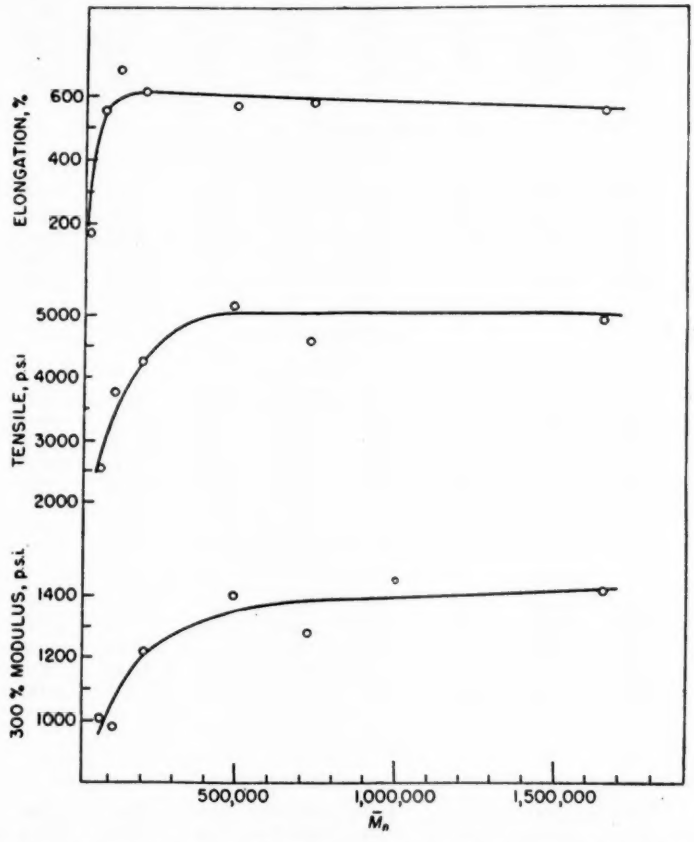

FIG. 5.—Stress-strain properties versus $\bar{M}_n$ for Fractions 1–6 cured 75 minutes with 1.75 parts of sulfur.

maximum tensile at break of 210 lbs. per sq. in., with a corresponding elongation of 167 per cent, and Fractions 8 and 9 were not vulcanizable with 1.75 parts of sulfur. No cures were obtained on Fraction 9 compounded with 15 and 40 parts of sulfur. A cure was obtained for Fraction 8 with 12.00 parts of sulfur, with resulting tensile strength of 1230 lbs. per sq. in. and an elongation of 140 per cent for a curing time of 45 minutes at 280° F.

A plot was made in Figure 5 of the tensile and elongation values at break and the 300 per cent modulus values *vs.* the number-average molecular weights

TABLE III

EFFECT OF CURING TIME AND SULFUR RATIO ON THE STRESS–STRAIN PROPERTIES OF VULCANIZATES OF GR-S FRACTIONS AT 280° F*

Fraction No. 1

Curing time (minutes)	300% modulus	Tensile strength	Elongation (%)	300% modulus	Tensile strength	Elongation (%)	300% modulus	Tensile strength	Elongation (%)
	Sulfur 0.75			Sulfur 1.00			Sulfur 1.75		
30	300	400	694	290	1300	740	520	2670	753
45	500	2800	814	450	2540	834	880	4830	687
60	530	3210	780	750	3810	720	1210	5090	566
75	530	3440	807	760	4400	720	1420	4980	566
150	640	3730	727	820	4060	654	1470	5070	498

Fraction No. 2

Minutes		Sulfur 1.0			Sulfur 1.2			Sulfur 1.75	
30	250	700	720	380	2080	760	690	3780	780
45	380	1480	767	780	4180	714	900	4420	807
60	520	2770	773	860	4000	674	980	4300	600
75	590	3150	813	890	4060	674	1240	4600	594
150	650	3260	753	980	4100	633	1260	4400	540

Fraction No. 3

Minutes		Sulfur 1.0			Sulfur 1.4			Sulfur 1.75	
30	270	580	673	610	3350	800	650	4080	760
45	550	3970	814	1070	4870	707	1180	5080	626
60	690	4210	753	1090	5300	660	1500	4980	534
75	720	4440	747	1020	4820	613	1400	5180	580
150	800	4280	700	1180	5200	620	1480	5080	540

Fraction No. 4

Minutes		Sulfur 1.5			Sulfur 1.75			Sulfur 2.0	
30	600	3300	833	410	2220	774	610	3870	734
45	600	3410	814	780	3980	726	1080	4720	674
60	940	3960	740	980	4200	680	1230	4950	607
75	910	4310	694	1210	4280	614	1300	4820	580
150	980	4400	654	1200	4220	567	1420	4600	520

Fraction No. 5

Minutes		Sulfur 1.75			Sulfur 2.25			Sulfur 2.75	
30	500	1850	727	750	3400	754	720	3200	713
45	790	3500	740	1170	3940	654	1240	4150	620
60	890	3780	726	1200	3340	520	1400	4180	567
75	910	3800	694	1340	3610	574	1550	4450	520
150	960	3660	668	1400	3650	533	1600	3280	387

Fraction No. 6

Minutes		Sulfur 1.75			Sulfur 2.5			Sulfur 3.0	
30	480	1020	507	700	2280	661	810	2540	607
45	780	1980	567	1210	3320	567	1280	1980	400
60	880	2680	687	1320	3680	594	1550	3200	473
75	1040	2580	567	1500	3500	507	1670	3130	440
150	900	2850	620	1410	2980	480	1860	2700	360

TABLE III—*Continued*

Fraction No. 7

Minutes	Sulfur 1.75		Sulfur 3.0			Sulfur 6.0	
30	No cure		—	340	207	—	1160	274
45	140	127	—	720	274	—	1710	274
60	100	107	—	980	300	—	1700	220
75	210	167	—	980	267	—	1950	267
150	120	153	—	1000	259	—	1940	214

Fraction No. 8

Minutes	Sulfur 1.75	Sulfur 12.0		
30	No cure	No cure		
45	No cure	—	1230	140
60	No cure	—	1070	114
75	No cure	—	1250	114
150	No cure	—	1290	120

Fraction No. 9

Minutes	Sulfur 15.0	Sulfur 40.0
30	No cure	No cure
45	No cure	No cure
60	No cure	No cure
75	No cure	No cure
150	No cure	No cure

Unfractionated GR-S (X-55)

Minutes	Sulfur 1.75		
30	300	2400	940
45	580	3210	807
60	760	3580	734
75	880	3600	668
150	940	3840	661

* In this tabulation 300 per cent modulus and tensile strength values are expressed as pounds per square inch; the values for sulfur represent parts per hundred parts by weight of rubber.

of the unmilled fractions. These fractions were cured for 75 minutes with 1.75 parts of sulfur in the tread-type recipe. These data illustrate graphically that the tensile strength increased linearly with increasing molecular weight, and tended to reach a limiting value when the number-average molecular weight of about 400,000 was reached. Fractions 1–5 had tensile strengths higher than that (3660) obtained on the unfractionated GR-S sample. Likewise, the percentage elongation at break increased linearly until a $\bar{M}_n$ of approximately 200,000 was reached. The first six fractions had elongations at break ranging from 560 to 690 per cent, compared to the value of 660 per cent for the unfractionated GR-S. The 300 per cent modulus values increased in a similar manner and reached a limiting value of 1350 at a $\bar{M}_n$ of approximately 500,000. The modulus values of the first six fractions were higher than that (880) obtained for GR-S.

A plot of the optimum stress–strain data (tensile strength, elongation, and 300 per cent modulus) *vs.* parts sulfur for the indicated optimum curing time of 75 minutes demonstrated the sulfur ratios that should be used to obtain vulcanized stocks having 300 per cent modulus values of 1000 lbs. per sq. in. As indicated in Figure 6 the parts of sulfur required to give these stocks increased as the molecular weight of the uncompounded rubber decreased.

A plot made of the maximum tensile strength in the range of sulfur values employed demonstrated that higher tensile strengths were obtained for Fractions 6 through 1 than that obtained on the GR-S sample. Here, also, the tensile strengths tended to reach a limiting value after a $\bar{M}_n$ of about 400,000 was reached. The percentage elongation at break remained reasonably constant at approximately 600 for fractions with $\bar{M}_n$ above 200,000 and the corresponding 300 per cent modulus values were all above 1200 lbs. per sq. in.

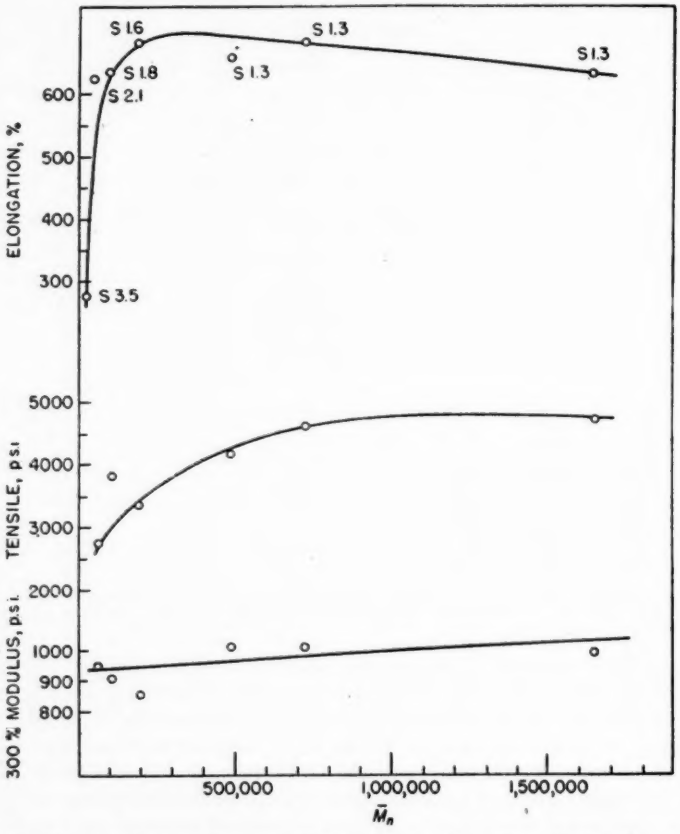

FIG. 6.—Stress–strain properties versus M_n for optimum sulfur ratios, using Fractions 1–6.

Additional quantities of the fractions were compounded by the compounding technique previously described and using the indicated optimum sulfur ratios. Cured physical test data, such as stress–strain, flex-life ratings, hysteresis, percentage Schopper rebound, percentage initial compression, Durometer hardness, and percentage permanent set, were obtained for Fractions 1–7 and also for the unfractionated GR-S sample. These data are summarized in Table IV.

The first six fractions comprising 72 per cent by weight of the original butadiene-styrene copolymer were cured to 300 per cent modulus values of 1000 ± 50 lbs. per sq. in. and had tensile strengths and elongations at break

PHYSICAL PROPERTIES OF VULCANIZATES OF GR-S (X-55) FRACTIONS IN THE SANTOCURE RECIPE

Property measured	1	2	3	4	5	6	7	X-55
M_n	1,650,000	724,000	482,000	193,000	103,400	65,800	23,600	
Sulfur (%)	1.3	1.3	1.3	1.6	1.8	2.1	3.5	1.75
300% modulus, p.s.i.								
75-min. cure	880	900	900	750	810	950	—	650
150	990	1010	1010	850	910	780	—	1000
Tensile strength (lbs. per sq. in.)								
75	4300	3600	4580	4680	3000	2760	1140 at 287%	3770
150	4750	4570	4150	3360	3850	4000	1100 at 273%	2940
Elongation (%)								
75	687	660	740	740	687	627	287	780
150	640	687	661	687	641	727	273	594
Durometer hardness								
75	55	55	56	55	59	64	—	56
150	56	56	57	57	60	64	69	59
Schopper rebound (%[a])								
75	60	58	58	58	42	40	—	38
150	62	59	60	58	42	40	35	40
Initial compression (%)								
75	22.5	24.4	24.4	23.1	25.3	22.6	No sample	29.5
150	23.4	23.8	24.4	23.1	25.1	24.2	23.4	27.2
ΔT, ° F[f]								
75	73	83	82	79	85	88	No sample	73
150	59	62	62	66	76	86	—	52
Permanent set (%)								
75	20.5	24 min.[b]	22.6	Blow out	18 min.[b]	13 min.[b]	—	24.0
150	11.5	12.3	13.3	13.0	18 min.[b]	12 min.[b]	3 min.[c]	20.8
Flexures								
75	2,710,000	780,000	1,190,000	760,000	1,030,000	290,000	180,000[d]	1,030,000
75	1,030,000	790,000	790,000	4,460,000	760,000	260,000	100,000[d]	650,000
150	680,000	600,000	1,130,000	670,000	350,000	290,000	70,000[e]	270,000
150	650,000	540,000	490,000	780,000	290,000	150,000	40,000	390,000
Quality index								
75	14.5, 6.5 → 10.5	—	5.98, 3.9 → 4.9	—	—	—	—	6.9, 4.1 → 5.5
150	6.5, 6.2 → 6.4	5.25, 4.75 → 5.00	10.0, 4.3 → 7.2	5.3, 6.1 → 5.7	—	—	—	3.1, 4.6 → 3.8

[a] Rebound taken on ¾-inch piece (hysteresis pellet).
[b] Minutes to blow out.
[c] Minutes to break up.
[d] Broke at rating of 7.
[e] Broke at rating of 5.
[f] Goodrich hysteresis at 212° F.

equal to, or greater than, that obtained on the unfractionated sample. These data indicate that Fractions 7, 8, and 9 must have had an adverse effect on the above-mentioned stress–strain properties of this copolymer.

Quality index values (a balance between Goodrich hysteresis and crack growth ratings) have been recently suggested by Juve[5] to be a useful indication of the tire tread performance. If the quality indices obtained at the two cures employed are averaged, the higher molecular fractions (1–4, which comprised 50 per cent of the unfractionated sample) had quality indices superior to that obtained for the unfractionated copolymer.

Quality index values were not obtained for Fractions 5–7, for the hysteresis pellets blew out before completion of the tests. Starting with Fraction 5, as the molecular weight of the fractions decreased, the blow-out time decreased. This occurred regardless of the fact that these fractions were cured to equivalent 300 per cent modulus values. If high Goodrich hysteresis values are related in some measure to poor tire tread performance, it is readily seen that the presence of these low molecular-weight vulcanizable fractions would have an adverse effect on tread quality.

Due to the lower molecular weights and to the larger proportions of sulfur required to cross-link effectively these molecules to give vulcanizates having 300 per cent modulus values of 1000 lbs. per sq. in., a more rigid network structure results with low molecular weights between points of cross-linking. These more rigid structures should have greater Durometer hardness values, and the data show that at equivalent 300 per cent modulus values the Durometer hardness values increased as the molecular weight decreased. This behavior is orthodox in view of the more rigid network obtained.

Similarly, for equivalent 300 per cent modulus values, the percentage Schopper rebound decreased as the molecular weight decreased. The values obtained for the first five fractions comprising 62 per cent of the original sample were much higher than that observed for the unfractionated GR-S specimen, and some of these were in the range obtained for natural rubber samples. Varying the curing time from 75 to 150 minutes did not have a measurable effect on the percentage rebound values of Fractions 4–7.

Qualitatively, the initial compression values on Fractions 1–7 were the same, and lower than the values obtained for the GR-S sample. This is attributed to the presence of a larger proportion of low molecular material in the unfractionated sample, namely, Fractions 8 and 9, with respective $\bar{M}_n$ values of 12,000 and 4000, and comprising 20 per cent of the unfractionated sample.

SOL–GEL PROPERTIES OF GR-S FRACTION BEFORE ADDITION OF CARBON BLACK

Experimental data thus far presented have indicated that the stress–strain and quality index values for the fractions which were cured to similar modulus values improved as $\bar{M}_n$ increased and tended to level off when $\bar{M}_n$ values of approximately 400,000 were reached for the raw copolymer fraction. It is evident that the molecular weight and the molecular-weight distribution of the fraction at the time of vulcanization is really the important factor which influences various physical properties of the vulcanizates of these fractions. Accordingly, a few experiments were conducted to determine the sol–gel properties of the fractions before the addition and subsequent dispersion of carbon black during the customary milling operations. These data are presented in Table V.

TABLE V

SOL–GEL PROPERTIES OF FRACTIONS OF GR-S (X-55) BEFORE ADDITION OF CARBON BLACK

Fraction	Gel (%)	Swelling index	$[\eta]_0$	Calculated $\bar{M}_n$
1	4	—	2.24	303,000
2	4	—	1.95	246,000
3	10	135	1.92	240,000
4	2	—	1.61	184,000
5	1	—	1.16	112,000
6	0	—	0.90	75,000
7	0	—	0.54	35,000
X-55	0	—	1.52	167,000

Cold milling of Fractions 1 and 2 rendered them gel-free in a short time. As the molecular weight of the original fraction increased, cold milling brought about greater percentage reduction in molecular weights, as indicated by $[\eta]_0$ measurements. For example, the unmilled Fractions 1 and 4 had molecular weights, respectively, of 1,650,000 and 193,000 for the sol portions, whereas just before the addition of carbon black the calculated $\bar{M}_n$ values for the fractions were, respectively, 303,000 and 184,000. Minor changes were observed for the lower molecular fractions. The sol–gel conditions before the addition of carbon black in the milling operation gave a better approximation to the sol–gel picture in the fractions at the time of vulcanization.

The smaller difference in calculated $\bar{M}_n$ of the first four fractions tends to explain the previously mentioned behavior of stress–strain properties as a function of $\bar{M}_n$.

In Figure 7 stress–strain data are plotted against the calculated number-average molecular weight of the milled fractions for Fractions 1–6, which were cured in a Santocure recipe using optimum sulfur ratios. As $\bar{M}_n$ increases, percentage elongations at break level off at a $\bar{M}_n$ value of about 200,000, and the tensile strength values tend to increase less rapidly when a $\bar{M}_n$ value of approximately 300,000 is reached.

Using the calculated molecular weight values listed in Table V for the milled fractions, a linear plot was obtained when $1/M$ was plotted *vs.* tensile values.

EFFECT OF NUMBER-AVERAGE AND WEIGHT-AVERAGE CONTRIBUTIONS TO THE PHYSICAL PROPERTIES OF GR-S

In the expressions:

$$Y = \sum w_i X_i \qquad Z = \sum n_i X_i$$

where X_i = physical property of fraction, w_i = weight percentage of fraction, n_i = number percentage of fraction, Y and Z, respectively, represent a given physical property of a heterogeneous sample, such as tensile strength, elongation, etc., that has been obtained by weight averaging or number averaging the corresponding physical property values obtained for the components of the sample.

Stress–strain properties, which have been obtained by weight and number averaging as described above, are listed in Table VI for the fractions which had been cured 75 minutes, using a Santocure tread-type recipe with 1.75 parts of sulfur. Fractions 7, 8, and 9 were considered to be essentially nonvulcanizable under the conditions, and should be expected to act essentially as a diluent in the unfractionated GR-S sample.

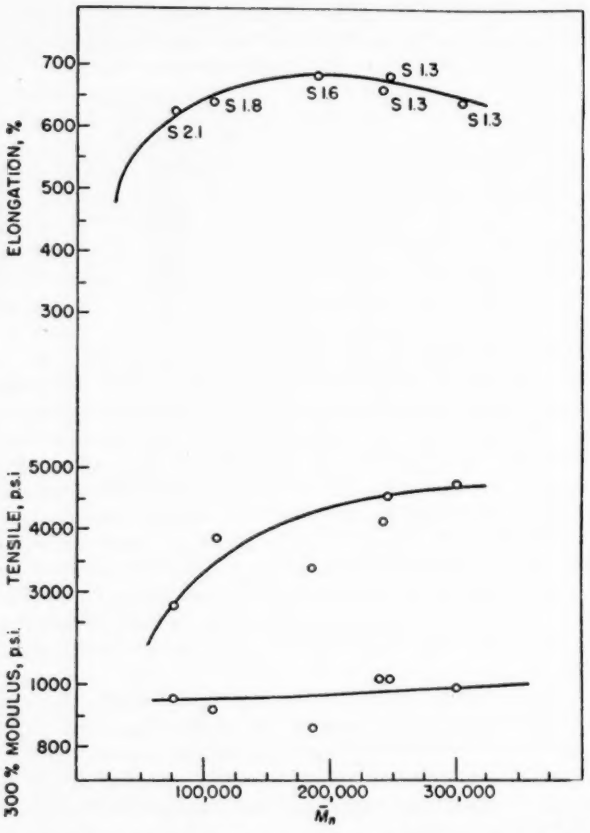

FIG. 7.—Stress-strain properties versus $\overline{M}_n$ for optimum sulfur ratios, using milled Fractions 1–6.

As indicated in Table VI, the best checks on the stress–strain properties obtained for the unfractionated GR-S sample were obtained by number-averaging the stress–strain properties of the first six fractions (unmilled), which are considered to be incorporated in the cross-linked network. The next best checks on these stress–strain properties were obtained by number-averaging the stress–strain properties of milled Fractions 1–6.

TABLE VI

WEIGHT-AVERAGE AND NUMBER-AVERAGE CONTRIBUTIONS TO PHYSICAL PROPERTIES OF GR-S

Fractions employed	Tensile strength ($\Sigma w_i T_i$) (lbs. per sq. in.)	Elongation ($\Sigma w_i E_i$) (percentage)	300% modulus ($\Sigma w_i M_i$) (lbs. per sq. in.)	Tensile strength ($\Sigma n_i T_i$) (lbs. per sq. in.)	Elongation ($\Sigma n_i E_i$) (percentage)	300% modulus ($\Sigma n_i M_i$) (lbs. per sq. in.)
1–6[a]	4309	601	1218	3514	613	1070
1–9[a]	3109	434	887	209	37	64
1–6[b]	4309	601	1218	3875	606	1139
GR-S	3600	668	880	3600	668	880

[a] Mol. wt. of unmilled fraction was used.
[b] Mol. wt. of milled fraction, before addition of carbon black, was used.

If weight-averaging and number-averaging are performed on the nine fractions, with zero contributions assigned to Fractions 7, 8, and 9, the tensile strength and elongation data and 300 per cent modulus value obtained by weight-averaging check reasonably closely with the values obtained on the unfractionated GR-S sample.

PERCENTAGE SHRINKAGE OF COMPOUNDED GR-S FRACTIONS

Compounded stocks (of the fractions and of GR-S, Santocure recipe without the sulfur) were milled at approximately 20° C, and the initial and the percentage shrinkage values after 10 minutes were measured at room temperature. These data are listed in Table VII.

TABLE VII

PERCENTAGE SHRINKAGE OF COMPOUNDED STOCKS OF GR-S FRACTIONS

Sample	Initial percentage shrinkage	Percentage shrinkage after 10 minutes
X-55	32	52
Fraction 1	22	42
2	30	50
3	26	49
4	26	48
5	18	38
6	11	32
7	Less than 11[a]	Less than 32[a]
8	Too soft to measure	Too soft to measure
9	Too soft to measure	Too soft to measure

[a] Excellent film; however, because of its low molecular weight, it elongated under little stress when removed from the roll. On standing for 10 minutes, no measurable shrinkage occurred.

Qualitatively, the initial and the percentage shrinkage values after 10 minutes at room temperature decreased with decrease in molecular weight. Processing improved, from the standpoint of ease and rate of pigment incorporation and smoothness of film and film edge, as the molecular weight decreased, and reached a limiting value of practically no measurable shrinkage for the seventh fraction.

PERCENTAGE STYRENE CONTENT OF GR-S FRACTIONS

Using the refractive index method of Madorsky and Wood[6], the percentage bound styrene values were determined for the fractions and the unfractionated copolymer. These data are listed in Table VIII. Excluding the values obtained for Fraction 9, the percentage bound styrene increased in a qualitative manner with increase in the molecular weights of the fractions.

Considering the fact that the percentage of styrene entering the butadiene-styrene copolymer changes (increases appreciably with increasing conversion)[11], and also considering the disappearance of the chain terminator (commercial dodecanethiol) and its effect on molecular weight, one might reasonably expect to find a regular increase in styrene content with increasing molecular weight of the copolymer fractions obtained from a GR-S sample prepared to 75 per cent conversion. However, the differences in styrene content encountered in our experimental work between the low and the high molecular fractions are rather small, which indicates the presence of copolymer molecules with varying styrene contents in a given fraction. It would be interesting to obtain further evidence of molecular structural heterogeneity in these fractions.

TABLE VIII

STYRENE CONTENT OF GR-S FRACTIONS BY REFRACTIVE INDEX[a]

Sample	Air-oven drying	
	n_D^{25}	Styrene content
X-55	1.5342	23.06
Fraction 1	1.5359	25.14
2	1.5355	24.65
3	1.5357	24.89
4	1.5353	24.40[b]
5	1.5341	22.94
6	1.5346	23.55
7	1.5340	22.82
8	1.5335	22.21
9	1.5353	24.40

[a] A minimum of 2 samples was used to obtain n_D^{25}. On each sample five readings were taken. All readings were then calculated for 25° C, and averaged. The correction for temperature was 0.000034 decrease in reading for each degree centigrade increase. The equation used for determination of styrene content was:

$$S = 22.94 + 0.122(n_D^{25} - 1.5341) \times 10^4$$

[b] Sample was dried for fifteen hours at reduced pressure at 25° C.

EFFECT OF $\bar{M}_n$ ON MOONEY VISCOSITY VALUES

Another problem of interest pertaining to the GR-S fractions was to determine the relationship between $\bar{M}_n$ and the Mooney viscosity values for gel-free samples. These Mooney values[12], designated as ML-4-212° F, are those which are obtained on the Mooney viscometer, using the large rotor at 4 minutes at 212° F. Sufficient quantities of the fractions employed in this investigation were not available for this study; however, fractions were available which had been obtained from another large-scale fractionation of the same GR-S (X-55) sample, and therefore Mooney viscosity values were obtained on some of these fractions.

From the experimental data listed in Table IX, it is evident that for the gel-free samples having $[\eta]_0$ of 1.37 and 0.80, which corresponds to molecular weights of 144,000 and 63,500, ML-4-212° F values of 30 and 5, respectively, were obtained.

The higher molecular samples having appreciable gel contents, and molecular weights above 250,000, gave very high Mooney readings with the small rotor. Granulation of the sample, which leads to false Mooney values, increased as a function of the gel content of the fraction. It is unfortunate that gelation does occur in these butadiene-styrene copolymers so readily, for it would be interesting to obtain the relationship between Mooney viscosity

TABLE IX

SOL-GEL PROPERTIES VERSUS MOONEY VALUES OF LARGE-SCALE FRACTIONATION OF GR-S (X-55)

Fractionation No. 1

Fraction	Percentage gel	Swelling index	$[\eta]$	ML-4-212° F
2	76	101	4.07	172[a]
3	62	102	2.10	160[a]
6	0	—	1.37	30
7	0	—	0.80	5

[a] ML-4-212° F, calculated by multiplying small rotor readings by 1.8.

and $\bar{M}_n$ values over a large molecular weight range for gel-free samples, and to obtain the contribution of each fraction to the resultant value of the unfractionated GR-S sample.

SUMMARY

A large-scale precise fractionation of GR-S (X-55) was carried out at 25° C, using a fractional precipitation technique. Nine fractions, each weighing approximately 150 grams and comprising about 11 per cent by weight of the original unfractionated sample, were obtained, with number-average molecular weights varying from 4000 to 1,650,000.

High molecular fractions undergo gelation rapidly, even when dried in the absence of light at reduced pressure, and the higher the molecular weight of the fraction, the greater the amount of gel formed. Compared to unfractionated butadiene-styrene copolymers of similar gel contents, the gel portions of the higher molecular fractions had unusually high swelling indices, indicating qualitatively that the average molecular weights between points of effective cross-linking in the three-dimensional gel structure were higher than those found in the past in unfractionated samples of similar gel contents.

Through the concentration range studied, the intrinsic viscosity values varied as a straight-line function of the concentration terms for all the fractions. However, the negative slopes of these lines increased as the molecular weight of the fraction increased, demonstrating the greater dependence of the intrinsic viscosity values of the higher molecular fractions on the concentration variable.

The relationship between number-average molecular weight, as determined by osmometric measurements, and limiting intrinsic viscosity of the GR-S fractions is given by the equation: $[\eta]_0 = 5.4 \times 10^{-4} M^{0.66}$, which is similar to that obtained by French and Ewart[10]. The μ_i values calculated from the equation of Huggins were essentially the same (0.35) through the molecular range 12,400 to 723,000.

Using 1.75 per cent sulfur (based on the rubber) in a Santocure tread-type recipe, only Fractions 1–6 were vulcanizable. The tensile strengths increased linearly with increase in molecular weight, and tended to reach a limiting value when the number-average molecular weight of about 400,000 (unmilled sample) was reached. Likewise the percentage elongation at break increased linearly until a $\bar{M}_n$ value of about 200,000 for the unmilled fraction was reached. The first five fractions had higher tensile strengths than the tensile strength of the unfractionated GR-S sample. The first six fractions had elongations at break ranging from 560 to 690 per cent, compared to the value of 660 per cent for the unfractionated sample. The 300 per cent modulus value increased in a similar manner with increasing molecular weight ($\bar{M}_n$), and reached a limiting value of 1350 lbs. per sq. in. at a $\bar{M}_n$ value of approximately 500,000 for the unmilled fraction.

The parts of sulfur per hundred parts of rubber required to give vulcanizates of Fractions 1–7 with 300 per cent modulus values of 1000 lbs. per sq. in. increased as an inverse function of molecular weight.

For equivalent 300 per cent modulus values as the molecular weight increased, the Goodrich hysteresis and Durometer hardness values decreased and the percentage Schopper rebound, tensile strength, elongation at break, quality index, and flex rating values tended to increase. Lower initial percentage compression values were obtained for Fractions 1–7, compared to the unfractionated GR-S sample.

Cold milling brought about greater percentage reductions in molecular weights (as indicated by $[\eta]_0$ measurements) as the molecular weight of the unmilled fraction increased. For example, Fractions 1 and 4 had $\bar{M}_n$ values of 1,650,000 and 193,000, respectively, for the sol portions, whereas when the samples were cold-milled to the time before the addition of carbon black the calculated $\bar{M}_n$ values were 330,000 and 184,000, respectively. The latter data are considered to give a better approximation of the molecular weights of the fractions at the time of vulcanization than the values obtained on the unmilled fractions.

For samples cured 75 minutes at 280° F, using 1.75 per cent sulfur, good checks were obtained on the stress–strain properties of unfractionated GR-S by a summation of the number-average contributions of the stress–strain properties of the first six fractions ranging in $\bar{M}_n$ from 1,650,000 to 65,800.

As the molecular weight increased, the percentage initial and percentage shrinkage values after 10 minutes (at room temperature) of compounded milled GR-S fractions increased and processing became poorer.

For the first eight fractions, the bound styrene content increased slightly as a function of increasing molecular weight. GR-S fractions having calculated $\bar{M}_n$ values of 144,000 and 63,500 had ML-4-212° F (Mooney viscosity) values of 30 and 5, respectively.

SYNOPSIS

A large-scale precise fractionation of GR-S (X-55) was performed using the fractional precipitation technique at 25° C. Nine fractions, each weighing approximately 150 grams and comprising approximately 11 per cent by weight of the original unfractionated sample, were obtained, and a detailed study was made showing the effect of number-average molecular weight and related sol–gel properties on various physical and chemical properties of the crude and vulcanized fractions. Using a Santocure tread-type recipe, preliminary compounding work indicated the sulfur ratios required to give vulcanizates with 300 per cent modulus values of 1000 lbs. per sq. in. All fractions were recompounded using these indicated optimum sulfur values. Generally, as the number-average molecular weight increased, better stress–strain and quality index data were obtained. These and other physical properties of the vulcanizates of these fractions are discussed in detail. As found in past fractionation studies pertaining to unsaturated high polymers, the higher molecular weight fractions, obtained from the unfractionated sample which was totally soluble in benzene, undergo considerable gelation when isolated and vacuum dried at 25° C in darkness. As the indicated molecular weight of the fraction increased, higher percentage gel contents were obtained. Compared to unfractionated butadiene-styrene copolymers of similar gel contents, the gel portions of the higher molecular weight fractions had unusually high swelling indices, indicating qualitatively that the average molecular weights between points of effective cross-linking in the three-dimensional gel structure were higher than those encountered in the past in unfractionated samples of similar gel contents. Other data are given pertaining to these fractions, such as the bound styrene content, percentage shrinkage of the compounded unvulcanized stocks, and the rate of gel breakdown on cold milling.

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REFERENCES

[1] Flory, *Ind. Eng. Chem.* **38**, 417 (1946).
[2] Flory, *J. Am. Chem. Soc.* **65**, 372 (1943).
[3] Juve and Schroeder, *India Rubber World* **115**, 501 (1947).
[4] Shearer, *India Rubber World* **116**, 491 (1947).
[5] Juve, *Ind. Eng. Chem.* **39**, 1494 (1947).
[6] Madorsky and Wood, U. S. Bureau of Standards, private communication, Sept. 14, 1944.
[7] Atm. $= hd_1$ (76 × 13.6), where h is the rise in osmotic pressure in cm. of benzene at 25.00° C, and d_1 is the density of benzene in grams per cc. at 25.00° C.
[8] Flory, *J. Chem. Physics* **10**, 51 (1942).
[9] Huggins, *J. Phys. Chem.* **42**, 911 (1938); **43**, 439 (1939); *J. Am. Chem. Soc.* **64**, 1712, 2716 (1942).
[10] French and Ewart, *Ind. Eng. Chem. Anal. Ed.* **19**, 165 (1947).
[11] Borders, A. M., Goodyear Tire & Rubber Co., private communication Dec. 28, 1942; Baker, W. O., and Heiss, J. H., Bell Telephone Laboratories, private communications, Mar. 23, 1943 and June 24, 1943.
[12] Mooney, *Ind. Eng. Chem. Anal. Ed.* **6**, 147 (1934); Taylor, RUBBER CHEM. TECH. **19**, 319 (1946).

PLASTICIZATION OF NATURAL AND SYNTHETIC RUBBERS. II. GR-S*

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INTRODUCTION

The work described here is a continuation, devoted to GR-S, of that already reported[1], and was designed to show the effects of each of the factors involved in normal plasticizing treatments, viz., heat, oxidation, mechanical working, addition of softener or of peptizing agent, on the plastic characteristics—softness, form of stress-flow relation, and elastic recovery—of the GR-S. The data so obtained will help in producing plasticized GR-S having the most suitable rheological characteristics for particular factory processes. The importance of thus being able to control these characteristics according to the process in view has been discussed elsewhere[2], and only a few typical cases need be quoted in illustration: (1) for extrusion or calendering, the stock should have a low recovery so that extruded material shall be smooth and have as nearly as possible the dimensions of the die, and calendered sheet a thickness equal to the calender nip width as well as freedom from curling at the edges; (2) for tubed articles, a stock possessing a high effective viscosity at low stresses or else a yield value (stress below which flow is negligible) helps to prevent their deforming under their own weight especially during open-steam vulcanization; (3) a soft stock is advantageous where processing involves very rapid deformation (as in some cable-covering extruders) to avoid excessive heat generation and scorching; (4) a rubber which, like GR-S, shows highly anomalous flow, *i.e.*, rate of deformation increasing much more than proportionately to the deforming force, deforms mainly near the walls of an orifice through which it is extruded, and the resultant stresses set up in the outer layers may well be the cause of tearing in extruded GR-S stocks; similarly, in extruding a section having thick and thin portions, stresses result from the big difference in extrusion rate between these portions, again leading to tearing.

Owing to the necessity, during the war period when the work was undertaken, of obtaining quickly some fundamental ideas on plasticization of GR-S, the work could not be carried out with the thoroughness that could have been desired, and for this reason no extensive theoretical interpretation of the observed effects has been attempted at this stage. The results are, however, of direct practical interest and form a useful basis for further work on the important subject of plasticization of rubbers in general.

EXPERIMENTAL

TREATMENTS INVESTIGATED

The plasticizing and other treatments investigated are summarized in Table 1. The peptizing agents selected for Treatment 3 have already been recommended[3]. In Treatments 2 and 3, using Batch CC, readings of the cur-

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TABLE 1

SUMMARY OF TREATMENTS INVESTIGATED

	GR-S Batch B	GR-S Batch CC
Details of GR-S used		
Date of recipe and type	July, 1943; not known	Dec., 1943; CC.¶
Benzene solubility at 35° C	46–56%	100%
Weight of gel§ per gram	30–35 grams	0.5 gram
Plastometer thickness (5 min. compression)	2.8–3.1 mm.	2.15 min.
Treatments		
1. *Cold milling;* cold water passing through rolls		
Mill*	I	II
Weight of batch	200 grams	220 grams
Temperature of GR-S	34° C after 20 min.	27° C after 10 min.
Periods**	10, 20, 40, 80 min.	10, 20, 70 min.
2. *Hot milling;* steam passing through rolls		
Mill	I	II
Weight of batch	200 grams	220 grams
Initial roll temperature	83° C	113° C
Batch temperature	102°–107° C	113°–116° C
Periods	10, 20, 40, 80 min.	10, 20, 68 min.
3. *Hot milling with peptizing agent;* B.P.H. = benzaldehyde-phenylhydrazone; I.N. = iron naphthenate		
Mill	II	II
Weight of batch	200 grams	220 grams
Initial roll temperature	113° C	111°–113° C
Batch temperature	116°–117° C	(*a*) & (*c*) 112°–116° C (*b*) 106°–112° C
Peptizing agent	1% B.P.H.	(*a*) 1% B.P.H. (*b*) 5% I.N. (*c*) 2% I.N.+0.5% B.P.H.
Periods	10, 20, 30, 40, 43 min.	10, 20, 65 min.
4. *Cold mastication in internal mixer*†; water-cooled		
Weight of batch	500 grams	—
Final batch temperature	about 70° C	—
Periods	5, 10, 20, 60 min.	—
5. *Hot mastication in internal mixer;* steam at 100° C passed through rotor		
Weight of batch	500 grams	—
Batch temperature	probably 130° C	—
Periods	5, 10, 20, 60 min.	—
6. *Heating in vacuo*‡	4 hr. at 150° C	—
7. *High-pressure oxidation*‡		
Oxygen pressure	60 lb. per sq. in.	—
Temperature	70° C	—
Periods	1, 3, 6, 12 days	—
8. *Thermal oxidative softening*‡		
Oxygen pressure	15 lb. per sq. in.	—
Temperature	125° C	—
Periods	1, 2, 4 hours	—
9. *Softener*‡		
Percentage of oil calculated on total mixture	5.9, 10.3, 31.5%	—

NOTES.—* *Mill I:* 6 × 12-in. rolls; surface speeds 37.5 and 55 ft. per min.; friction ratio 1.46; nip 0.03 in.; distance between guides 5¼ in. *Mill II:* rolls 6 × 12 in. and 7.2 × 12 in.; surface speeds both 44 ft. per min.; friction ratio 1.00; nip 0.03 in.; distance between guides 5 in. ** A small portion was removed for test after each period. † Size B Bridge-Banbury. ‡ *See* text for details of procedure. ¶ Made by United States Rubber Co., Institute, W. Virginia. § Weight refers to benzene-swollen gel remaining from solubility test.

rent consumption by the mill motor showed no significant differences between batches with and without peptizing agent.

For the *heating in vacuo* (Treatment 6), plasticity test-cylinders, 11 mm. diameter by 11 mm. high, were heated in a high vacuum. During the heating drops of liquid condensed on the cooler parts of the vessel; these were apparently fat acid volatilized from the GR-S. As this loss might affect the plasticity, similar experiments were made with acetone-extracted GR-S.

For *high-pressure oxidation* (Treatment 7), the GR-S was sheeted 2 mm. thick and subjected to oxygen at a moderate temperature in the oxygen bomb. Three days' oxidation gave appreciable tackiness, and six days a very tacky product. In contrast, acetone-extracted (and hence antioxidant-free) GR-S gave a friable, leathery, nonthermoplastic product, with little elasticity.

The *thermal oxidative softening* (Treatment 8) was based on the German procedure for Buna-S, using air at 4–4½ atm. To obtain a similar oxygen concentration without using pressure, the GR-S, sheeted 2 mm. thick, was heated in circulating oxygen at atmospheric pressure; one hour's treatment gave a very soft tacky product, but after four hours, although still soft, it was no longer tacky.

For *incorporation of softener* (Treatment 9), the GR-S was passed twice between warm tightly closed rolls to form a sheet. Weighed pieces of this were soaked in mineral (spindle) oil for various periods, and then, together with an untreated blank, kept for 24 hours at room temperature and four hours at 40° C, and finally reweighed.

MEASUREMENT OF PLASTICITY, RECOVERY, AND SOLUBILITY AND SWELLING IN BENZENE

Plasticity by shearing-cone plastometer[4].—With this instrument it is possible to measure, during any desired period of time, the shear stress in rubber subjected to any of the following constant shear rates: 0.01, 0.1, 1.0, 10 reciprocal seconds (*i.e.*, 0.012, 0.12, 1.2, and 12 r.p.m. of the rotor). Tests were made at 90° C. With milled GR-S a difficulty arises from the variation of the shear stress with time, the initially high value falling rapidly during the first few seconds and then more slowly but apparently never becoming constant. If, after a period of rest, the GR-S is sheared a second time, the stress is found to have increased again by an amount depending on the rest period, but the initial high value is not regained. Raw GR-S and GR-S plasticized by means other than milling do not show this behavior, and the stress in some cases increases slightly with time.

Owing to this dependence on time, the following procedure was adopted: the GR-S is sheared at rotor speeds of 1.2, 0.012, 0.12 and 12 r.p.m. successively, for periods of 10, 4, 4, and 1 minutes, respectively, the shear stress being measured at the end of each period.

In many cases the shear rate and shear stress could be related by a simple power law:

$$\text{rate of shear} = (F/c)^n \qquad (1)$$

where F = shear stress, c = consistency, n = a positive numerical constant. (The practical significance of n has been fully discussed[1].) Sometimes, however, there were signs of a yield value, as exemplified in the graph for 70 minutes'

hot mastication in Figure 6, which shows a selection of the observed stress/shear-rate relationships plotted on logarithmic scales.

Plasticity by parallel-plate (Williams) plastometer.—Tests were made at 90° C, using 1-cc. cylindrical specimens (11 by 11 mm.) and a 5-kg. load, readings being taken at short intervals up to 30 minutes' compression. The stress/shear-rate relation was deduced from these readings by the method of Scott[6], and in many cases Equation (1) was obeyed over the range of shear rates studied. The values of n so obtained were not always identical with those obtained more directly by the shearing-cone plastometer. This may be because the power law, Equation (1), holds only over a limited stress range (as later work[6] indicates) and the parallel-plate plastometer works at lower shear rates than the shearing-cone plastometer. The values of n used in the figures and discussion are those from the former instrument, since these are more complete than the shearing-cone data.

Recovery.—This was measured by two methods. (1) *Parallel-plate recovery.*—At the end of the parallel-plate plasticity test (above) the specimen was allowed to recover for 24 hours at 90° C, and its thickness remeasured. This method has the disadvantage that dissimilar materials are not compressed under the same conditions, since soft ones undergo a larger strain; accordingly, the following additional method was used, in which both the amount and the rate of straining are constant, so that conditions are more like those in, say, calendering and extruding. (2) *Constant-strain recovery.*—Specimens 11 mm. square and 8 mm. thick were compressed uniformly during 5 seconds to 1.6 mm. thickness, held compressed for 5 seconds, and then allowed to recover for 5 minutes and the thickness remeasured; temperature 70° C. In both methods the recovery (increase in thickness) is expressed as percentage of the compression (decrease in thickness).

Solubility and swelling in benzene.—0.1 gram of GR-S was left in contact with 30 cc. benzene at 35° C for 16 hours, following the method described by Sebrell[7]. The "gel" referred to in the tables and discussion is the weight of benzene-swollen gel per gram of original GR-S.

RESULTS

Figures 1–5 show the changes in the following properties during mastication on the mill or in the internal mixer [graphs (*a*) and (*b*)] or with increasing oxidation periods or softener content [graph (*c*)]: Figure 1: plastometer thickness (parallel-plate plastometer, 5 minutes compression); Figure 2: effective viscosity (stress corresponding to unit shear rate in shearing-cone plastometer; this instrument was not completed in time for experiments on Batch B); Figure 3: value of n in plastic flow relation, Equation (1); Figure 4: parallel-plate recovery (measured on parallel-plate plastometer specimen); Figure 5: constant-strain recovery (by constant-strain test). In Figures 1–5 the broken-line parts of the curves are only approximate, since no experimental points were obtained on them. Figure 6 gives a selection of logarithmic shear stress/shear strain graphs for GR-S treated by the various methods (shearing-cone plastometer).

The benzene solubility and swelling data for the treatments represented in Figures 1–5 are given in Table 2; results of the vacuum heating experiments are in Table 3 (below).

TABLE 2

BENZENE SOLUBILITY AND SWELLING TEST

"Swelling" = g. benzene absorbed by 1 g. of (dry) gel, calculated from the "gel" and "solubility" figures. No results were obtained for Treatments 6 and 9 of Table 1.

GR-S batch	Solubility (%)		Swollen gel (g. per g. original GR-S)		Swelling	
	B	CC	B	CC	B	CC
1. *Cold milling*						
Nil	46	100	30.8	0.2	56	—
10 min.	100	99	0.0	0.6	—	60
20 min.	100	—	0.0	—	—	—
70 min.	—	88	—	0.3	—	2
80 min.	100	—	0.0	—	—	—
2. *Hot milling*						
Nil	46	—	34.7	—	63	—
10 min.	47	—	19.5	—	36	—
20 min.	51	96	—	0.4	—	9
70 min.	—	94	—	0.4	—	6
80 min.	55	—	13.5	—	29	—
3. *Hot milling with peptizing agent*						
1% B.P.H. 10 min.	—	98	—	0.3	—	16
20 min.	—	97	—	0.5	—	16
70 min.	—	88	—	0.7	—	5
5% I.N. 10 min.	—	93	—	0.4	—	4
20 min.	—	94	—	0.4	—	6
65 min.	—	96	—	0.4	—	8
2% I.N. + 10 min.	—	95	—	0.5	—	8
0.5% B.P.H. 20 min.	—	99	—	0.6	—	55
60 min.	—	98	—	0.5	—	25
4. *Cold mastication in internal mixer*						
60 min.	100	—	0	—	—	—
5. *Hot mastication in internal mixer*						
60 min.	55	—	6.4	—	13	—
7. *High-pressure oxidation*						
Nil	56	—	30.4	—	68	—
3 days	54	—	35.2	—	75	—
6 days	56	—	37.6	—	85	—
8. *Thermal oxidative softening*						
Nil	52	—	12.5	—	25	—
1 hour	65	—	21.2	—	60	—
2 hours	40	—	28.5	—	47	—
4 hours	39	—	30.2	—	49	—

TABLE 3

EFFECT OF HEATING *in vacuo* AT 150° C FOR 4 HOURS

	Plastometer thickness (parallel-plate 5 min. compression) mm.		Parallel-plate recovery (%)		*n* in power-law Equation (1)*	
	before heating	after heating	before heating	after heating	before heating	after heating
Normal GR-S	2.90	3.56	49	82	—	—
GR-S, acetone-extracted	3.48	4.57	—	95	4.6	7.5
GR-S, acetone-extracted and cold-milled 20 min.	2.41	3.48	8	83	2.4	6.2

* Values are approximate because results deviate from the power law; with normal GR-S this deviation was so great that no valid figure could be given.

Abbreviations in Figures 1–5: CM = cold milling; HM = hot milling; CB = cold internal mixer (Banbury); HB = hot internal mixer; HMP = hot milling with peptizing agent (benzaldehyde-phenylhydrazone (B.P.H.) unless otherwise stated; I.N. = iron naphthenate); TOS = thermal oxidative softening.

(a)

	Batch CC; Mill II		
	CM	HM	HMP
Temp. (° C)	27	113–116	106–116

(b)

	Batch B				
	CM	HM	HMP	CB	HB
Mill	I	I	II	—	—
Temp. (° C)	34	102–107	116	70	130±

(c) Batch *B*

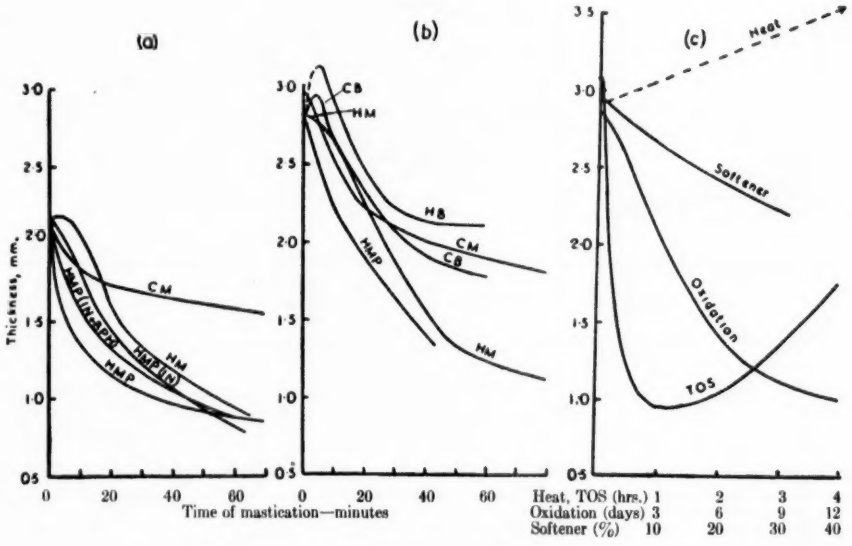

FIG. 1.—Plastometer Thickness (5 minutes in Parallel-Plate Plastometer).

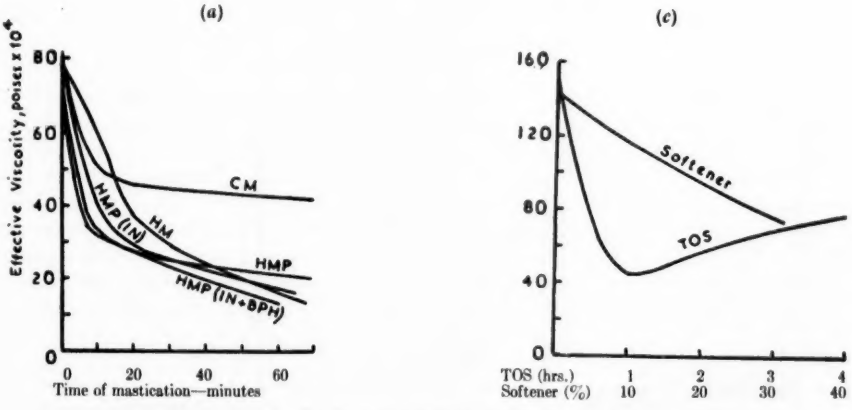

FIG. 2.—Effective Viscosity (Shearing-Cone Plastometer).

Abbreviations in Figures 1–5: CM = cold milling; HM = hot milling; CB = cold internal mixer (Banbury); HB = hot internal mixer; HMP = hot milling with peptising agent (benzaldehyde-phenylhydrazone (B.P.H.) unless otherwise stated; I.N. = iron naphthenate); TOS = thermal oxidative softening.

(a)
Batch CC; Mill II

	CM	HM	HMP
Temp. (° C)	27	113–116	106–116

(b)
Batch B

Mill	CM I	HM I	HMP II	CB —	HB —
Temp. (° C)	34	102–107	116	70	130±

(c)
Batch *B*

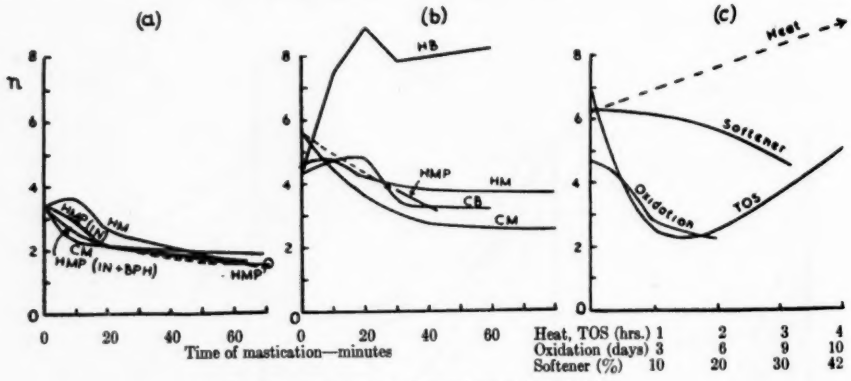

FIG. 3.—Value of n in Power Law of Plastic Flow.

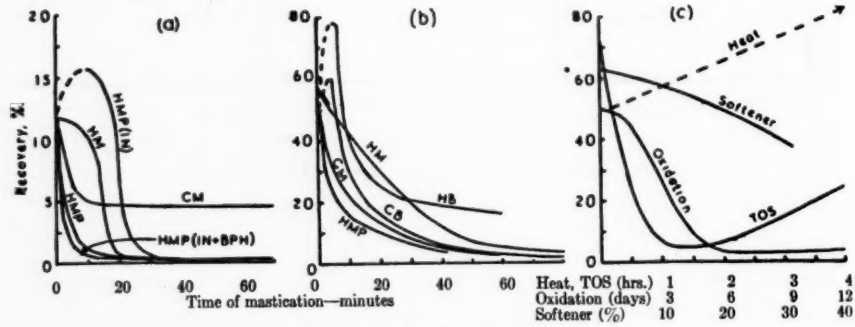

FIG. 4.—Parallel-Plate Recovery.

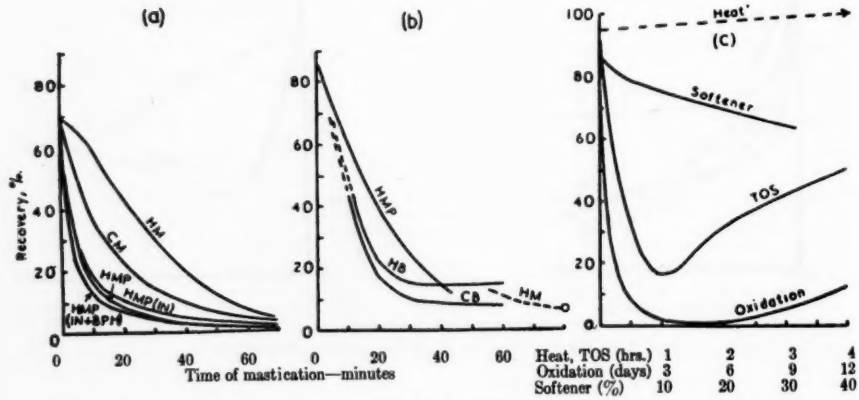

FIG. 5.—Constant-Strain Recovery.

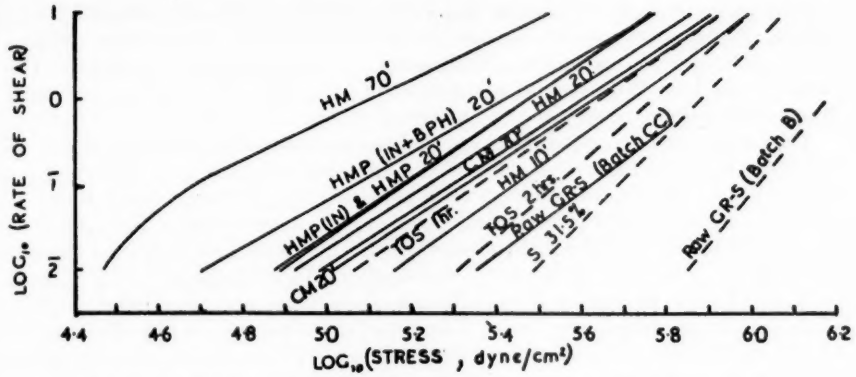

FIG. 6.—Relation between Shear Stress and Shear Rate (Shearing-Cone Plastometer). (S = Softener)

EFFECTS PRODUCED BY THE VARIOUS TREATMENTS

MILLING (ROLL MILL)

The experiments without peptizing agent will be discussed first. Cold milling progressively reduces the plastometer thickness reading, effective viscosity, n value, and recovery, all these changes being most rapid during the first 10–20 minutes (see Figures 1–5, graphs (*a*) and (*b*)).

Hot milling (102°–116° C) produces qualitatively similar effects, except that the first few minutes have increased the n values (see Figures 3 (*a*) and (*b*)). This increase is perhaps one manifeststion of what appears to be a fundamental difference between the hot and cold treatments, namely, that initially hot milling is less effective than cold milling in giving a soft product with low recovery and n value, but after a time the positions are reversed, and the hot treatment becomes the more effective; thus it comes about that the "hot" and "cold" curves often cross over, as in Figures 1 (*a*) and (*b*), 2 (*a*), 3 (*a*) and (*b*), and 4 (*a*), though some of the recovery curves, Figures 4 (*b*) and 5 (*a*), do not show this, cold milling giving the lower recovery at all milling times. Since short milling times, say, up to 20 minutes, are generally of most technical interest, these results show clearly the advantages of cold over hot milling (at 102°–116° C) when no peptizing agent is used.

The reason for the reversal in effectiveness as between hot and cold treatments is probably that breakdown of the GR-S occurs in two ways, by oxidation and by mechanical rupture of the chain molecules (the latter by analogy with natural rubber[1]. Oxidation, being a chemical reaction, is greatly accelerated by high temperature, whereas mechanical breakdown is favored by low temperatures where the rubber is stiff, so experiences bigger shear stresses when passed between the rolls. In the early stages of milling, while the rubber is stiff, mechanical breakdown apparently predominates, and so cold milling is the more effective; but as the rubber becomes softer, less mechanical breakdown occurs, whereas oxidation continues undiminished, so hot milling finally becomes the more effective. The fact that hot milling involves more oxidation than cold is shown by oxygen estimation[8]; 80 minutes' cold milling did not significantly increase the oxygen content, whereas 80 minutes' hot milling increased it by 0.4 per cent (this may be compared with 0.5 per cent increase during 6 days in oxygen at 60 lb. per sq. in. and 70° C).

The partially benzene-soluble Batch B is made completely soluble by cold milling, whereas hot milling does not do this, and indeed reduces the swelling of the gel fraction, suggesting that some cross-linking has occurred. The solubility and swelling results for Batch CC are inconclusive, because it is almost completely soluble in the untreated state.

Peptizing agents used during hot milling increase the softening effect, as shown by both plastometer thickness and effective viscosity [see Figures 1 (*a*) and 2 (*a*)], so 10 minutes' milling with peptizing agent is equivalent to 15–30 minutes without. Of the peptizing agents tried, 1 per cent of benzaldehyde phenylhydrazone (B.P.H.) is the most effective, and 5 per cent iron naphthenate the least (in previous experiments[1], working at 100° C instead of 113° C as in the present experiments, iron naphthenate showed no peptizing effect). Peptizing agents also help to reduce recovery and the *n* value, and the effect on the former can be very great, 10 minutes' milling with a peptizing agent being equivalent to 40–50 minutes without (see Figure 5 (*a*); these experiments, on Batch CC, suggest that the iron naphthenate-B.P.H. mixture reduces recovery most effectively.

In Figures 1 (*a*), 2 (*a*), and 3 (*a*) there is evidence that after long milling *e.g.*, 60–70 minutes, the peptizing agent loses its effect; GR-S hot-milled for such long periods, either with or without peptizing agent, had considerable tackiness and had to be scraped off the mill rolls. Peptizing agents did not appear to affect the solubility of Batch CC GR-S.

A technically interesting comparison is that between hot milling with a peptizing agent and cold milling without; Figures 1–5 show that milling at 102°–116° C (or preferably perhaps an even higher temperature) with B.P.H. or an iron naphthenate-B.P.H. mixture gives a soft, low-recovery material more quickly than cold milling, though the latter seems better if a low *n* value is needed.

MASTICATION IN INTERNAL MIXER

The data in Figures 1–5, graphs (*b*), show that after a short initial period, during which some stiffening and increase in recovery may occur [Figures 1 (*b*) and 4 (*b*)], mastication in the internal mixer softens progressively GR-S and reduces its recovery. The plastometer thickness results, Figure 1 (*b*), show cold mastication to be more effective than hot in softening the GR-S; the shearing-cone plastometer was not completed when these experiments were made, but Mooney values were determined[9] on 60-minute masticated samples, namely, cold, 35; hot, 29, showing hot mastication to be the more effective. This apparent contradiction is due to the parallel-plate plastometer working at a lower shear rate (not above 0.07 sec.$^{-1}$) than the Mooney (about 0.8 sec.$^{-1}$); as the processing of rubber usually involves high shear rates, the advantage in technical practice would appear to lie with hot mastication, if advantage is judged solely by softness.

On the other hand, hot mastication is less effective than cold in reducing elastic recovery, and whereas the latter reduces the *n* value, hot mastication increases it up to the very high figure of 8 or 9, giving a material that is almost rigid under very small forces but deforms readily under large forces. Moreover, whereas cold mastication makes the GR-S completely soluble in benzene, hot mastication has little effect and appears to reduce the swelling of the gel fraction (Table 2); this suggests that high temperature has caused cross-linking, which would also account for the high *n* value. For all properties other than softness, therefore, cold mastication is better than hot.

It is clear that by varying the temperature at which the GR-S is worked in the internal mixer, especially if a bigger range than the 70° C to 130° C used in these experiments is attainable, a wide variation in plastic behaviour can be obtained, thus illustrating the possibility of making plasticized GR-S suited to particular processes. On the other hand, accidental temperature variations introduce serious variability in processing.

HEATING IN VACUO

GR-S, whether acetone-extracted or not, becomes considerably less plastic on heating for four hours at 150° C *in vacuo*, and the recovery and n value increase (see Table 3); these effects appear greatest in the acetone-extracted and milled sample. In keeping with their high recovery values, the heated samples were elastic and resilient. Similar results have been obtained with Buna-S, and in this case more drastic heating (330° C) carried the changes to an extreme, giving a hard nonplastic material[1].

The heated GR-S showed decreased solubility in benzene (exact quantitative tests were not made) and all the evidence suggests that heating causes cross-linking, giving an effect similar to scorching. This is in marked contrast to the behavior of natural rubber, which, when heated *in vacuo*, shows pronounced softening at 200° C upwards and a reduction of recovery and n value at 250° C upwards, and liquefies at temperatures much above 250° C.

HIGH-PRESSURE OXIDATION

Figures 1–5, graph (*c*), show that oxidation at 60 lb. per sq. in. and 70° C gives a progressive and very marked softening and fall in n value and recovery, apart from an apparent increase in constant-strain recovery at 12 days, perhaps due to an interruption of some weeks between the 6- and 12-day tests. Somewhat unexpectedly, in view of these effects, the oxidation did not much alter the benzene solubility or the swelling of the gel fraction (Table 2). A 6-day test with oxygen at 300 lb. per sq. in. and 70° C gave a softer product than that from any other treatment.

Oxidative plasticization of GR-S at 70° C and 60 lb. per sq. in., however, is a very slow process, since the period required to give the same effect as 20 minutes' cold mastication (using Batch B) ranges from 2 to 4 days, according to the property considered.

Removal of the antioxidant normally present in GR-S entirely alters the nature of the changes produced by oxidation. Acetone-extracted GR-S after 4 days in oxygen at 60 lb. per sq. in. and 70° C gave a friable, and inelastic product, and shorter tests failed to reveal any softening such as occurs when normal GR-S is used. The observation that oxidation may either harden or soften GR-S, according to the conditions, agrees with conclusions from the aging of the vulcanized material[10].

THERMAL OXIDATIVE SOFTENING

Figures 1–5, graphs (*c*), TOS curves, show that heating at 125° C in oxygen at 1 atm. produces during the first hour a considerable softening and reduction of recovery and n value, but that further treatment reverses these changes; at 4 hours there is some deviation from the power-law plastic flow relation. Benzene solubility (Table 2) shows analogous though small changes, namely, an increase followed by a decrease, and the swelling of the gel fraction appears to change similarly.

The hardening effect of excessive high-temperature oxidation was shown by a test at 150° C, which after 4 hours converted the GR-S into an inelastic resin.

Thermal oxidative softening combines heat and oxidation, which have opposite effects on GR-S, and it appears that in the initial states the oxidative effect predominates, since the changes observed resemble those of oxidation (see preceding section); while the later effects, resembling those of heating *in vacuo* (see above), can be ascribed to cross-linking induced by heat, a change which appears to be promoted by removal of the anti-oxidant.

SOFTENER

Incorporation of mineral oil without the use of heat or mechanical working produces some softening and reduction in recovery, but these effects are relatively small, and only the largest amount of oil (31.5 per cent on the mixture) noticeably reduces the n value. It is evident that to obtain a product with plastic characteristics even approaching those given, say, by cold milling or by hot milling with a peptizing agent, would need so much oil that the vulcanizate would have inferior mechanical properties. Oil-swollen GR-S may, however, be softened by milling so that it can be calendered and frictioned and possess sufficient tack for many purposes[11].

COMPARISON OF DIFFERENT PLASTICIZING TREATMENTS

Certain comparisons have already been mentioned in describing the effects of the individual treatments, but a fuller discussion of their relative merits is given in this section.

In the first place, heat alone, *i.e.*, in absence of oxygen or mechanical action, may be dismissed as having no plasticizing action whatever—indeed, just the reverse. Likewise, incorporation of mineral oil without any other treatment is so ineffective that it need not be further considered.

All of the other four treatments, namely, roll-milling, mastication in the internal mixer, high-pressure oxidation at 70° C, and thermal oxidative softening, soften GR-S, although, for making an extremely soft product, cold milling or hot or cold working in the internal mixer do not appear suitable (see Figures 1 (*a*), 1 (*b*), and 2 (*a*)). For rapid production of a moderately softened GR-S, roll-milling is better than the internal mixer, and hot milling with a peptizing agent, *e.g.*, B.P.H., is the best of the "mechanical", *i.e.*, milling or mastication, treatments; if it is desired to avoid the use of a peptizing agent, milling on cold rolls is the best.

Oxidative plasticization at 70° C and 60 lb. per sq. in. oxygen pressure is too slow for practical purposes; either the temperature or the oxygen concentration needs to be raised, and in keeping with this it is found that thermal oxidative softening at 125° C and 15 lb. per sq. in. is very effective, one hour or less giving as much softening as prolonged milling (compare graphs (*b*) and (*c*) in Figure 1).

Reducing the elastic recovery of GR-S is usually at least as important as making it soft. Figures 4 and 5 show that all the mechanical and oxidation treatments reduce recovery; cold working is always better than hot, other conditions being equal, but hot milling with a peptizing agent is quicker than cold milling without. There is no clear preference between the roll mill and the internal mixer.

The value of n, which represents the extent of deviation from ordinary viscous flow or, expressed otherwise, the sensitiveness to changes in the de-

forming force, is reduced by all the mechanical treatments except hot working in the internal mixer, which has the opposite effect; milling on cold rolls is the most effective. Oxidative treatments likewise can greatly reduce *n*.

Complete solubility in benzene seems to be best achieved by cold working either on the roll mill or in the internal mixer. Hot working (without peptizing agent) on rolls or in the internal mixer and the two oxidative treatments do not produce a soluble product from one which is initially only partly soluble.

The above summary shows that the same treatment does not necessarily give the best results for all the properties—softness, recovery, and *n* value. It follows that GR-S batches brought to the same softness in different ways are not identical, and it is, therefore, useful to consider what difference exists between them. Comparison on the basis of equal softness is, of course, not the only possible procedure, but it has been selected as convenient and as having been used in the work on natural rubber[1].

In Figures 7–9, recoveries and *n* values are plotted against the 5-minute parallel-plate plastometer reading, so materials on the same vertical line are of equal softness; curves for hot-milled natural rubber are included for comparison with the Batch B GR-S. The black spot represents the untreated GR-S, and arrows show the direction of increasing treatment, *i.e.*, longer periods of mastication or oxidation or increasing amount of softener. The broken-line parts of the curves are approximate, since no experimental points were obtained on them. The fact that all the GR-S curves on one graph do not start from the same point, as ideally they should, is due to the variability of the GR-S.

Figures 8 and 9, of which the latter is probably the more informative[12], show that different plasticizing treatments are not equivalent; thus, in Figure 9 (*b*), materials brought to the same plastometer reading of 2.0 mm. vary in recovery from 2 to 55 per cent. With the mill or internal mixer cold working usually, though not always, gives lower recovery (for the same plastometer thickness) than hot working, other things being equal; hot roll-milling seems to be especially unfavorable. If a peptizing agent is used in the latter process, however, recovery can be reduced more effectively, and in fact sometimes (Batch CC, Figure 9 (*a*) at least as well as by cold-milling.

The TOS and oxidation curves again show the adverse influence of high temperature, since thermal oxidative softening at 125° C is not so good as oxidation at 70° C and a higher oxygen pressure. Judged by Figure 9 (*b*) the latter seems quite effective, though still inferior to cold working on the mill or in the internal mixer. Incorporation of a softener without further treatment is not a good way of reducing recovery.

Figure 8 (*b*) shows that none of the treatments examined gives a product with the low recovery of natural rubber, a result in keeping with the greater difficulty of processing GR-S.

The *n* values plotted in Figure 7 again show that different treatments are far from equivalent, and that cold working (mill or internal mixer) is better than hot, assuming that a low *n* value, as is characteristic of natural rubber, is desirable; in contrast to recovery, however, hot working in the internal mixer is is now the least effective, indeed, worse than useless, and cold roll-milling is the best of these mechanical treatments. Peptizing agents used in hot milling give little or no advantage in *n* value. The conclusions regarding oxidative treatments are similar to those for recovery, except that oxidation at 70° C and 60 lb. per sq. in. now appears at least as effective as cold milling. Addition of softener, except perhaps in large amounts, is again of little use.

Abbreviations in Figures 7–9: CM = cold milling; HM = hot milling; CB = cold internal mixer (Banbury); HB = hot internal mixer; HMP = hot milling with peptizing agent (benzaldehyde-phenylhydrazone (B.P.H.) unless otherwise stated; I.N. = iron naphthenate); TOS = thermal oxidative softening.

(*a*)

	Batch CC; Mill II		
	CM	HM	HMP
Temp. (° C)	27	113–116	106–116

(*b*)

	Batch B				
	CM	HM	HMP	CB	HB
Mill	I	I	II	—	—
Temp. (°C)	34	102–107	116	70	130±

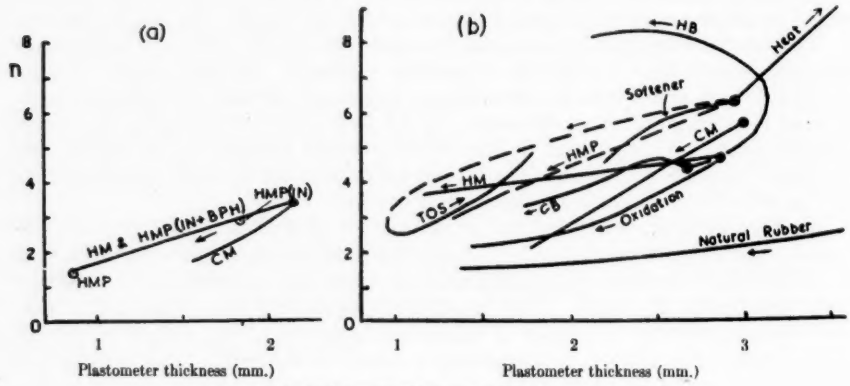

FIG. 7.—Relation between Plastometer Thickness and n Value.

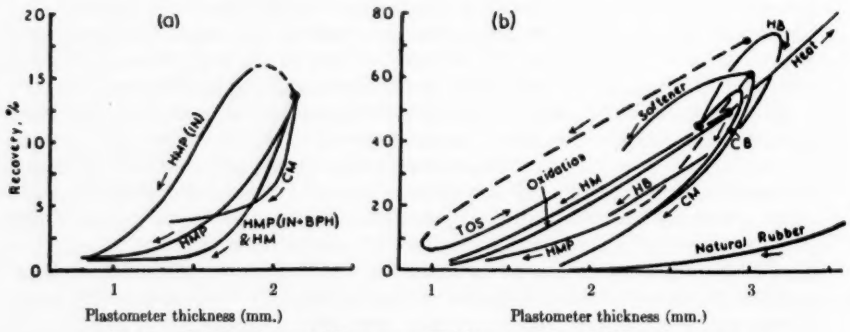

FIG. 8.—Relation between Plastometer Thickness and Parallel-Plate Recovery.

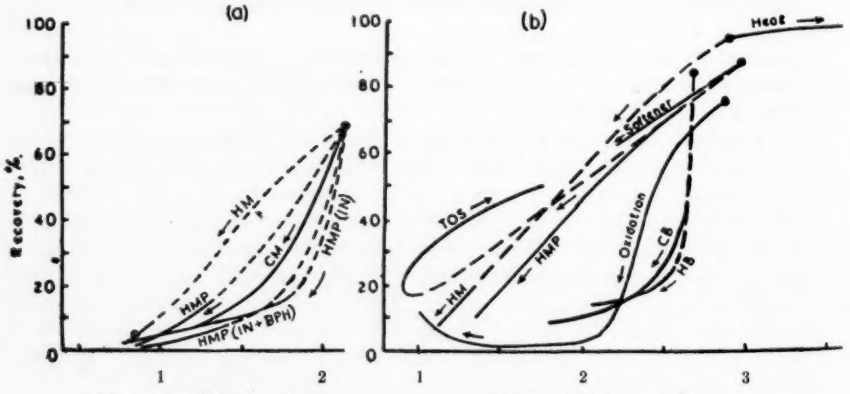

FIG. 9.—Relation between Plastometer Thickness and Constant-Strain Recovery.

The fact that GR-S batches plasticized by different methods have different n values means that of two batches one may be the softer at low rates of deformation but the stiffer at high rates; this is shown by the fact that the stress/shear graphs in Figure 6 sometimes cross over. An interesting feature of this figure is the general tendency of the lines to converge towards the top-right-hand corner, *i.e.*, at high shear rates. This tendency of different materials to behave more nearly alike as the shear rate (or stress) is increased has been observed also in a range of butadiene-styrene copolymers (American and German) and in ebonite stocks containing different reclaims, and merits further investigation as a matter of both theoretical and practical importance. In Figure 6 the upper part of the lines has been drawn straight, as it was then believed that they were straight; it is now realized, however, that these lines tend to curve upwards at the top end[6].

INFLUENCE OF PLASTICIZING TREATMENT ON PROPERTIES OF VULCANIZATE

To see whether plasticizing GR-S by the methods described above affected its properties after vulcanization, mixes comprising GR-S 100, EPC black 50, sulfur 2, zinc oxide 3, stearic acid 1, pine tar 3, mercaptobenzothiazole 1, and diphenylguanidine 0.25, were made from 600-gram lots of GR-S, Batch CC, previously treated as follows:

A: untreated
B: 40 minutes' milling on cold rolls
C: 80 minutes' milling on cold rolls
D: 10 minutes' milling on hot (about 115° C) rolls with 1% B.P.H.
E: 20 minutes' milling, as D
F: 60 minutes' thermal oxidative softening at 128° C, other conditions as described[13].
G: 120 minutes' thermal oxidative softening, as F.

For treatments B-E the even-speed Mill II (see Table 1) was used. The mixing of all the compounded batches was done on the cool rolls of this mill, and occupied 30–35 minutes.

The three types of treatment were chosen as being the most effective for plasticizing GR-S. The times were so chosen that B, D, and F should have as nearly as possible the same plastic properties, and similarly with C, E, and G; exact equivalence in all plastic properties is of course impossible, for the reasons discussed[14].

The following parallel-plate plastometer results were obtained on the mixed stocks:

	A	B	C	D	E	F	G
Plastometer thickness (mm.) after 5 minutes' compression	2.81	2.63	2.56	2.39	2.27	2.55	2.40
n	5.8	5.5	5.7	5.7	5.8	5.7	5.8

Hot milling with a peptizing agent (D, E) gave rather softer stocks than was anticipated, otherwise the three types of treatment gave roughly equivalent plastic properties.

The difference between the untreated (A) and the plasticized batches (B-G) of GR-S appears less in this compounded mix then in the uncompounded state as indicated by the data in Figures 1 (*a*), 1 (*c*), 3 (*a*), and 3 (*c*), though in view of the difference in plastic flow characteristics between the compounded and un-

compounded GR-S, an adequate comparison is not possible on the basis of the plasticity data available. In any further work on plasticizing treatments it will be important to see how far the differences introduced by different treatments persist after compounding with carbon black.

Table 4 gives the properties at optimum vulcanization. Standard test methods[15] were used except: (1) the tension set test used 15 minutes' stretching and 60 minutes' recovery; (2) aging was for 3 days in air at 100° C; (3) tear strength at 75° C by the A.S.T.M. crescent specimen[16]; (4) abrasion measured on the Akron machine[17], using 25° angle; (5) resilience by Lüpke pendulum at various temperatures; (6) cut growth test is essentially the De Mattia bend-flexing test[18] modified by puncturing the specimen, at the center of the groove, by a 0.05-inch diameter needle.

TABLE 4

PROPERTIES OF VULCANIZATES

Plasticizing treatment	Nil	Cold milling		Hot milling with B.P.H.		Thermal oxidative softening	
	A	B	C	D	E	F	G
Optimum vulcanization at 148° C (min.)	45	45	45	40	35	50	45
Tensile strength of dumb-bell specimens (lb. per sq. in.)	2980	3000	2660	2700	2520	2660	2440
Elongation at break (%)	630	650	580	620	590	610	610
Modulus at 300% (lb. per sq. in.)	910	950	960	910	830	850	890
British Standard Hardness No.	55	49	47	50	50	52	50
Tension set (%) after 200% elongation	5.8	6.0	5.5	5.0	5.0	5.5	6.0
Abrasion loss (cc. per 1000 revolutions)	0.56	0.56	0.54	0.54	0.63	0.55	0.58
Tear strength at 75° C (lb. per in. thickness)	300	315	310	290	295	270	270
Resilience (%) at 20° C	43	42	42	44	43	43	43
Temperature (° C) of minimum resilience	−27	−26	−29	−24	−26	−26	−27
Cut growth resistance (flexing kilocycles per cm. growth)	35	38	30	25	40	25	25
Properties after aging as % of unaged value:							
Tensile strength	78	78	82	78	79	82	90
Elongation at break	56	53	53	47	46	54	53
Modulus at 300%	225	215	210	235	275	230	215

Apart from a slight acceleration with B.P.H., vulcanization is unaffected by the plasticizing treatments.

Tensile strength, and possibly elongation and hardness number, appear to decrease slightly with plasticization, but the effect is no greater than experimental error, except perhaps with tensile strength in treatments E and G and hardness in treatment C.

As regards the other properties of the unaged rubbers, although some individual mixes appear to differ from the control mix A, *e.g.*, F and G in tear strength, and D, F, and G in cut-growth, the plasticizing treatment has never consistently produced an effect greater than the experimental error. This is true also of tear strength at room temperature, not recorded in Table 4.

Maintenance of tensile strength during aging is never impaired, but hot milling with B.P.H. appears to have aggravated the stiffening and loss of elongation. Exposure-cracking of the stretched vulcanizate was not significantly affected by any of the plasticizing treatments.

SUMMARY

Continuing the work described in Part I[1], experiments have been made to determine the separate effects of heat, oxidation, mechanical working on rolls or in an internal mixer, peptizing agents (used in hot milling), and absorption of softener on the softness, elastic recovery, and plastic flow relation (between applied force and rate of flow) of GR-S.

Heat alone, without oxygen or mechanical action, does not soften GR-S, but makes it harder and more elastic, presumably by inducing cross-linking of the chain molecules; GR-S thus differs fundamentally from natural rubber, which can be softened by heat. Absorption of softener (mineral oil) softens GR-S and reduces its recovery, but these effects are too small to form a practicable plasticizing method.

Either oxidation or mechanical working softens GR-S considerably, reduces its elastic recovery, and brings its plastic flow relation nearer to that of well masticated natural rubber, i.e., approaching ordinary viscous or Newtonian flow (flow rate proportional to stress). Peptizing agents such as benzaldehyde phenylhydrazone or iron naphthenate promote the effect of hot milling, presumably by accelerating oxidation, which is shown to occur during hot, but not appreciably in cold, milling.

Of the methods tried, those which plasticize GR-S most quickly are (1) hot milling with a peptizing agent, and (2) oxidation at 125° C and 15 lb. per sq. in. oxygen pressure; if the latter is continued too long, however, hardening sets in.

The results show that GR-S, like natural rubber, can be plasticized by mechanical breakage of the chain molecules by the shear stresses set up during mastication, as well as by oxidation, which presumably causes breakage of the molecules at the double bonds. Mechanical and oxidative treatments, however, do not give the same properties; mechanical breakdown in the cold gives a product completely soluble in benzene, whereas oxidation does not, and is less effective in reducing recovery, and there may be other differences not yet revealed. In view of these differences and the fact that heat has effects opposite to oxidation or mechanical working, it follows that the various possible ways of plasticizing GR-S, since they involve heat, oxidation, and mechanical action in different combinations and degrees, give plasticized batches with very different properties, even if the length of the treatments is so adjusted as to give, say, the same Williams or Mooney plasticity reading. These differences are fully discussed in the present paper; the main conclusions are:

(1) To reduce elastic recovery, mechanical working at low temperatures with the rolls or internal mixer water-cooled is generally best, though equally good results may be obtainable by hot roll-milling with a peptizing agent. Heating in air or oxygen is less satisfactory, especially if a high temperature, *e.g.*, 125° C as in the German procedure, is used.

(2) To produce GR-S with a plastic flow relation approaching that of natural rubber, it is important to avoid high temperatures, especially when access of air is limited, as in the internal mixer. Hence cold roll-mixing is the best method; oxidation at 70° C and 60 lb. per sq. in., although it gives a product similar to that of cold milling, is far too slow to be practical, and peptizing agents scarcely improve the effect of hot milling.

(3) None of the treatments examined gives to GR-S the plastic properties of natural rubber, since it always retains a higher recovery and deviates more from simple viscous flow.

(4) To make GR-S completely soluble, mechanical working appears essential, and cold working is best.

Attention is again drawn to the important effect of differences in recovery and plastic flow relation on the behavior of plasticized rubbers during processing in the factory, and examples are given.

Study of the flow characteristics of GR-S plasticized in different ways confirms a previous observation that, as the deforming force or rate of deformation increases, the various materials behave more nearly alike—a significant point in processing operations that involve very rapid deformations.

The effects of cold milling, hot milling with a peptizing agent, and thermal oxidative softening on the properties of GR-S after compounding with carbon black and vulcanizing were studied. The only adverse effects observed were somewhat more age-stiffening (increase in modulus and loss of elongation during 100° C air aging) as a result of hot-milling with a peptizing agent, and possibly a slight loss of tensile strength in this treatment and in thermal oxidative softening.

REFERENCES

[1] Piper and Scott, *J. Rubber Research* **16**, 151 (1947).
[2] Scott, *Trans. Inst. Rubber Ind.* **20**, 8 (1944).
[3] U. K. Ministry of Supply, Admiralty, Ministry of Aircraft Production. Services' Rubber Investigations, Manufrs. Memorandum No. M. 9, **1944**.
[4] Piper and Scott, *J. Sci. Instruments* **22**, 206 (1945).
[5] Scott, *Trans. Inst. Rubber Ind.* **7**, 169 (1931).
[6] Scott and Whorlow, Rubber Tech. Conf. London, **1948**, Preprint No. 7.
[7] Sebrell, *Ind. Eng. Chem.* **35**, 736 (1943).
[8] These were kindly carried out by the British Rubber Producers' Research Association, by a difference method based on carbon hydrogen combustion.
[9] These values were determined by the British Rubber Producers' Research Association.
[10] Scott, *Trans. Inst. Rubber Ind.* **21**, 78 (1945).
[11] U. K. Ministry of Supply, Admiralty, Ministry of Aircraft Production. Services' Rubber Investigations, Manufrs.' Memorandum No. M. 12, **1944**.
[12] See the paragraph on "Recovery" in the section on "Measurement of Plasticity, Recovery, and Solubility and Swelling in Benzene" in the present paper.
[13] See section on "Treatments Investigated" in the present paper.
[14] See section on "Comparison of Different Plasticizing Treatments" in the present paper.
[15] British Standards Institution, British Standard Method of Testing Vulcanized Rubber: B.S. 903–1940.
[16] American Society for Testing Materials. A.S.T.M. Designation D624-41T. We are indebted to the John Bull Rubber Co., Ltd., for these tests.
[17] Dawson and Porritt, "Rubber: Physical and Chemical Properties", Croydon, **1935**, p. 540.
[18] American Society for Testing Materials. A.S.T.M. Designation D430-40, Method B (b) Bend Flexing.

ELECTRICALLY CONDUCTING RUBBER *

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AVON INDIA RUBBER CO., LTD.

In recent years the dangers and inconveniences arising from the presence of static electrical charges on rubber conveyor belts, rubber flooring, rubber-tired vehicles and the like, have aroused interest in the use of electrically conducting rubber as a means of minimizing the accumulation of static electricity. Conventional rubber compounds, which have electrical resistivities normally above 10^7 ohm-cm. and as high as 10^{14}–10^{16} ohm-cm. for nonblack compositions[1], favor the accumulation of static charges. By using high loadings of channel black, the resistivity can be reduced considerably. If special types of carbon black are employed the resistivity can be reduced to a very low value; in fact, the development of a compound with a resistivity of 1 ohm-cm. has been reported[2]. A compound with a resistivity of about 10 ohm-cm., processible on ordinary factory-size rubber machinery, is described later in this paper. Rubber compounds with resistivities less than 10^7 ohm-cm. are generally grouped under the generic title of "electrically conducting rubbers".

The conduction of electricity through rubber-carbon black compositions is attributed to the ability of the carbon black to form chains of particles through the rubber[3]. The formation of these chains depends on the particle size, crystal structure, and degree of dispersion of the black[4]. The special types of black referred to above, termed conducting blacks, possess this ability for chain formation to an advanced degree.

The work described below deals with the compounding of conducting rubbers, their application, and the methods used for testing. It appears under three main headings: measurement of resistivity; development of highly conducting rubber; and development and testing of antistatic tires.

MEASUREMENT OF RESISTIVITY

Apparatus.—The measurement of the electrical resistance of a semiconductor is a difficult matter, and a study of the literature reveals that many different methods have been used by different workers. An improved method recently described by Newton[5] eliminates errors due to contact resistances (see below). This method and that used in these experiments are based on the same principle. In each case a current is caused to flow uniformly through a rubber sample, and the voltage gradient is measured between probes in the sample by means of a valve voltmeter.

In the method described here, the whole apparatus is built into a box and powered by the a.c. mains without supplementary batteries. Two valve rectifiers (*a*, *b* in the circuit diagram, Figure 1) are used to provide independent sources of high-voltage direct current. One of these provides the current through the sample, which is in the form of a rectangular block $15 \times \frac{1}{2} \times \frac{1}{2}$ inch, with tinfoil squares molded on to the end faces and wires molded in the

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middle at intervals of about 4 cm. If the supply terminals are shorted a current of about 7 milliamperes flows; if they are connected to the ends of a bar whose resistance is 300,000 ohms a current of 1 milliampere flows. The majority of samples take a current of about 6 milliamperes, representing a current density of about 4 milliamperes per sq. cm.

The second rectifier (*b*) provides the voltage for the plates of a triode valve (*c*), which can be adjusted by potentiometers (*d*, *e*). To measure the voltage gradient along the sample, the positive end is earthed and the grid lead, previously earthed, is connected to each of the probes in turn. This has the effect of unbalancing the triode valve circuit and balance is restored by applying an extra voltage by means of the potentiometer (*e*). This applied voltage is read directly on the voltmeter (*f*). As the potential on the grid is static and the input impedance of the triode is very high no current flows along the grid lead, i.e. the voltmeter takes no current from the sample, and so there is no error due to contact resistance of the probes.

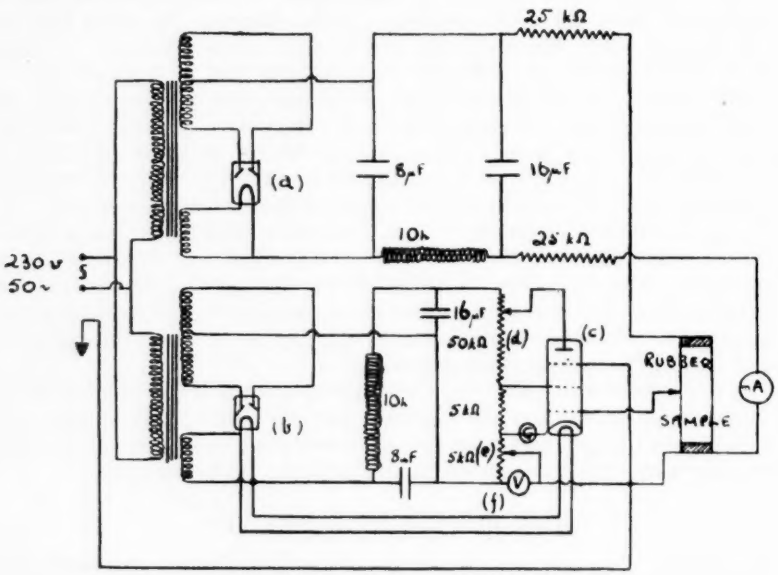


FIG. 1.—Apparatus for the measurement of resistivity.

As the instrument is worked from the a.c. mains and contains an earth lead, some leakage occurs through the insulation of the cable, transformer, etc., but the current in the voltmeter lead does not exceed 1×10^{-6} amp. Thus errors from this cause are negligible for resistivities less than 5×10^{4} ohm-cm., and for higher resistivities this method is not used because the range of the meters is not sufficiently great.

Method of test.—The vulcanized sample with molded-in plates and probe-wires is stored under conditions of constant temperature and humidity for 48 hours and then tested as described above. From the instrument direct readings of the current through the sample and of the potential difference between each probe and the end of the sample are obtained. From these figures the resistance along the bar to each probe is determined directly and a graph is drawn to

show the relation between resistance and distance. The gradient of the straight line obtained corresponds to the resistance per unit length of the bar and its intercepts with the axes are a measure of the contact resistance at the ends.

Typical graphs are shown in Figure 2, with readings in Table 1. From graphs such as these the specific resistance of the compound used may be determined.

For resistivities above 10^4 ohm-cm. an alternative method is used. Blocks are vulcanized 3 × 3 inches in area with thicknesses from ¼ up to 2 inches, with tinfoil sheets molded on the square faces. These blocks are connected to the

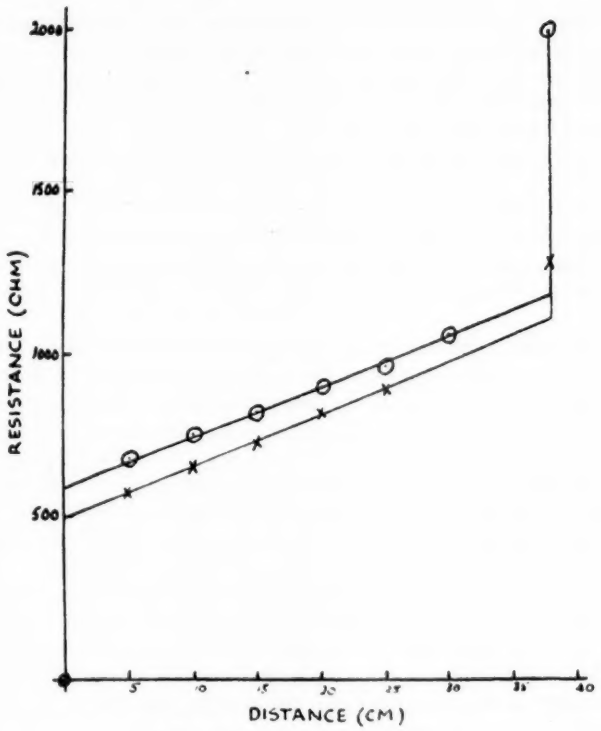


FIG. 2.—Typical conductivity graphs.

TABLE 1

TYPICAL RESISTIVITY RESULTS

No. of probe	Positive electrode	1	2	3	4	5	6	Negative electrode
Distance from end (cm.)	0	5	10	15	20	25	30	38
Potential (volts)	0	6.4	7.0	7.6	8.5	9.2	10.1	18.2
Current (milliamperes)	9.4	9.4	9.4	9.4	9.5	9.6	9.6	9.6
Resistance (ohms)	0	681	744	808	895	958	1051	1896

No. of probe	Positive electrode	1	2	3	4	5	Negative electrode
Distance from end (cm.)	0	5	10	15	20	25	38
Potential (volts)	0	5.7	6.5	7.2	8.1	8.9	13.1
Current (milliamperes)	9.9	9.9	10.0	10.0	10.0	10.1	10.1
Resistance (ohms)	0	576	650	720	810	882	1297

supply electrodes of the instrument and the current measured. The current is also measured when the electrodes are short-circuited.

	Current milliamperes	Total resistance ohms	Voltage
On short circuit	I_1	50,000	$50\ I_1$
With block connected	I_2	$50\frac{I_1}{I_2} \times 1000$	$50\ I_1$

$$\text{Resistance of block} = 50{,}000\ \frac{(I_1 - I_2)}{I_2}\ \text{ohms}$$

Knowing the resistance of the block, the contact resistance is ignored and the resistivity calculated from the dimensions of the block.

Effect of electrodes.—This latter method has the disadvantage that it takes no account of contact resistances. One of the greatest difficulties in the measurement of electrical resistivity has been the fact that the interface between rubber and any other material is highly resistant to the flow of electricity[5]. This means that in this method the resistance measured is the total resistance of the block and of the contact resistances between each of the tinfoil electrodes and the rubber block. However, in the experiments for which this method was used a high degree of accuracy was not required, and as most of the rubbers considered had resistivities below 1×10^4 ohm cm. the method was not often used.

Most of the measurements made by earlier workers make no allowance for the effect of contact resistance, and the method described by Newton[5] is the first important attempt to measure true resistivity. Earlier work depended on finding electrodes that did not give rise to high contact resistances, but neither mercury nor brass plates which have been extensively used in the past are suitable as electrodes. It has been claimed by Bulgin[6] that molded tinfoil electrodes are free from contact resistance, but such has not been found to be the case in the experiments described in this paper. It is believed, however, that these give less misleading results than other electrodes.

Effect of voltage.—Rubber, like most other semiconductors, does not obey Ohm's law and so the resistance varies with the applied voltage. Some workers have sought to overcome this by quoting the resistivity at a certain applied voltage. This is insufficient since it is the voltage gradient which actually affects the results, and this depends on the sample dimensions as well as on the applied voltage.

The equation [resistivity × current density = voltage gradient] does not involve sample dimensions, and if the resistivity varies with the voltage gradient it varies also with current density. It would seem, therefore, equally justifiable to quote resistivities at a given current density as at a given voltage gradient. This is done with the instrument described above, since all measurements are made with a current density of approximately 4 milliamperes per sq. cm.

However, Newton states[5] that electric saturation is reached when above a certain voltage gradient Ohm's law holds. It appears that the voltage gradient and not the current density is critical in attaining saturation. In these circumstances an ideal method would use a voltage gradient higher than that required for saturation for all samples, when the resistivities would be independent of voltage gradient.

Effect of test conditions. (*a*) *Errors of measurement.*—To compare figures obtained by the methods described above, it is necessary to know something of the errors involved and the effects on the conductivity of the samples of the various processing factors. Certain irreducible errors occur in the actual measurement of resistivity by means of the apparatus described above, the principal errors of measurement being: (1) distance (approx. 1 mm. in 5 cm.) 2 per cent; (2) current (not greater than 0.1 milliampere in 5–10 milliamperes) 1–2 per cent; and (3) voltage (for an accurate setting of the galvanometer the voltage may vary up to 0.3 volt), at 5 volts 6 per cent, and at 20 volts 1.5 per cent. Therefore, the resistance from the end to a given point may vary up to 10 per cent, although the mean error is about 5 per cent. The mean resistance along the sample is obtained with greater accuracy, and an inspection of a large number of actual length/resistance curves suggests that the errors in the results ascribable to errors of measurement do not exceed 3 to 4 per cent.

Experiments repeated on the same sample at different times gave results which showed that, apart from differences due to atmospheric conditions, there was a variability in the resistivity of the order expected from the above considerations. In addition, these preliminary experiments showed that the contact resistance differed in different experiments on the same sample and that variations in the atmospheric conditions appeared to affect the resistivity.

In the various experiments described in this section of the paper, different compounds were used and their compositions are given in Table 2.

TABLE 2

EXPERIMENTAL COMPOUNDS

Reference No.	I	II	III	IV	V	VI
Smoked sheet rubber	100	100	100	100	100	100
Acetylene black	60	60	60	—	—	45
Dixie Voltex	—	—	—	45	42.5	—
Zinc oxide	5	5	5	5	5	5
Stearic acid	2	2	2	2	3	2
Pine tar oil	3	3	3	3	2	3
Vulcaflex-B	—	—	—	—	1.25	—
Mercaptobenzothiazole	0.8	0.8	0.8	0.8	—	0.8
Benzothiazoyl disulfide	—	—	—	—	0.6	—
Sulfur	2	2	2	2	3	2

(*b*) *Effect of humidity.*—Experiments were arranged to investigate the effect of humidity on the resistivity of conducting samples. A mix of composition I was used to prepare two pairs of conductivity samples which were vulcanized at 280° F for 45 minutes. One of each pair was enclosed in an air-tight tin containing calcium chloride, the other in an air-tight tin containing water. The samples were left for four months at a constant temperature of 70° F, and then removed into a room kept at constant temperature (70° F) and humidity (67 per cent) and the conductivities measured. These measurements were repeated at intervals of 24 hours for a week. The results are shown in Table 3 and in Figure 3. It will be seen that the conductivity increases with moisture content and that it takes about 4–5 days for a sample initially saturated with water or thoroughly dried to reach equilibrium with its surroundings. In each of the pairs tested the resistivity of the dry sample was 30 per cent more than that of the moist sample. As a result of this experiment it was

TABLE 3

EFFECT OF HUMIDITY ON RESISTIVITY (OHM-CM.)

No. of days	0	1	2	7
A. Sample 1	36.5	35	32	29
B. Sample 1	25.5	26.5	27	29
A. Sample 2	57	55	53	50
B. Sample 2	40	44	47.5	50

(A after storing over calcium chloride; B after storing over water.)

decided that, in all subsequent tests, the samples should be kept at constant temperature and humidity for at least 48 hours before testing.

(*c*) *Effect of temperature.*—The temperature coefficient of resistivity of vulcanized rubber is appreciable[7], and so all the resistivity determinations described in this report were carried out at 70° F.

Effect of processing variations. (*a*) *Effect of direction of milling.*—Two main experiments were designed to show the effect on conductivity of the direction of milling. In the first, a rubber mix of composition II was sheeted out ¼ inch thick, and strips were cut in the direction of milling and perpendicular to this direction. These strips were used to build up conductivity samples in the usual way, and these were then vulcanized and tested. Graphs of resistance against position are shown in Figure 4, and two features are immediately obvious. First, the samples prepared from strips cut across the direction of milling show sudden discontinuities; secondly, there is no significant difference between the resistivities of samples prepared from strips cut in different directions. The reason for the discontinuities in the one pair of samples was attributed to the fact that these were built from strips placed end to end. The sheet had not been wide eough to cut strips 15 inches long across the sheet, so shorter strips had been used. Further experiments showed that, whenever a sample was built from short strips placed end to end, discontinuities in resistivity resulted.

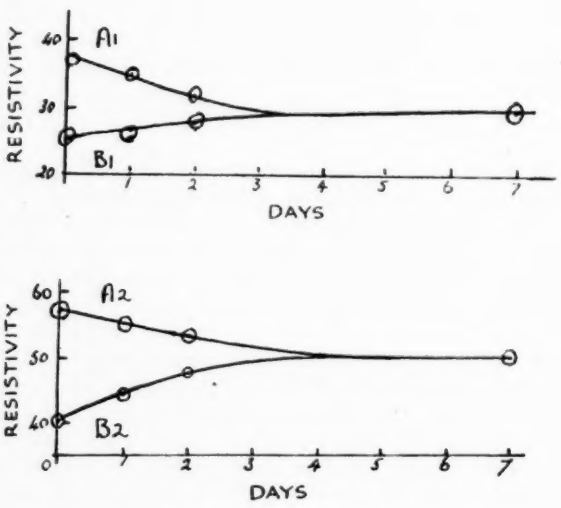


FIG. 3.—Effect of humidity.

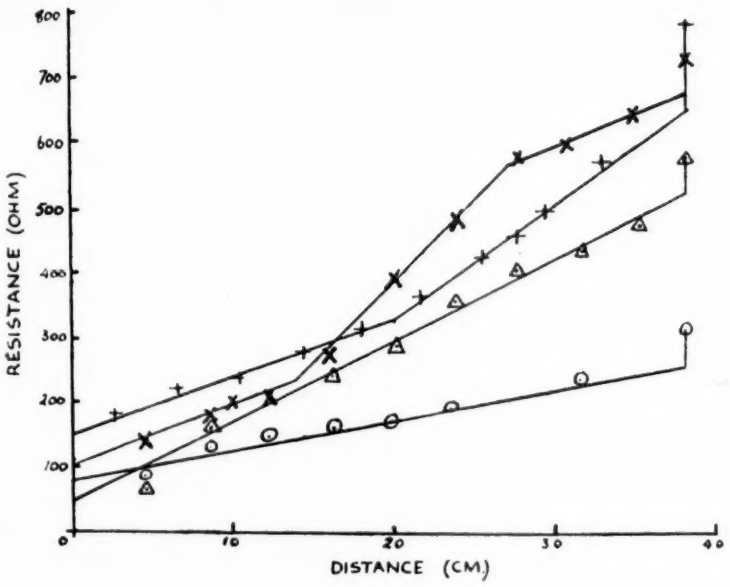


FIG. 4.—Effect of direction of milling: { ×−× } across direction of milling. { +−+ } { △−△ } along direction of milling. { ○−○ }

In the second experiment each sample was built as follows: two strips $5 \times \frac{1}{2}$ inch were cut from the $\frac{1}{4}$-inch thick sheet in the direction of milling and two similar strips in a perpendicular direction. Twenty $\frac{1}{2}$-inch squares were also cut. One strip cut in one direction was placed at one end of the mold and a strip cut in the other direction at the other end. The squares were piled up into a block $5 \times \frac{1}{2} \times \frac{1}{2}$ inch, and this was inserted between the strips. Wires were then inserted as usual and the remaining strips added. The resulting block was in three sections: first, with the direction of milling parallel to the length of the block; second, with the direction of milling vertical and, third, with the direction of milling across the width of the block. This is shown diagrammatically in Figure 5.

FIG. 5.—Composite block, to show effect of direction of milling.

Five such blocks were prepared, and the variation of resistance along the length of each block is shown graphically in Figure 6.

The following general conclusions about the effect of direction follow from these experiments: (1) strips cut from different parts of the same sheet have different resistivities when vulcanized; (2) strips cut across the direction of milling are slightly less resistant than those cut in the direction of milling, but the results obtained for the resistivity through the direction of milling are indeterminate; (3) these differences remain when a number of strips are molded

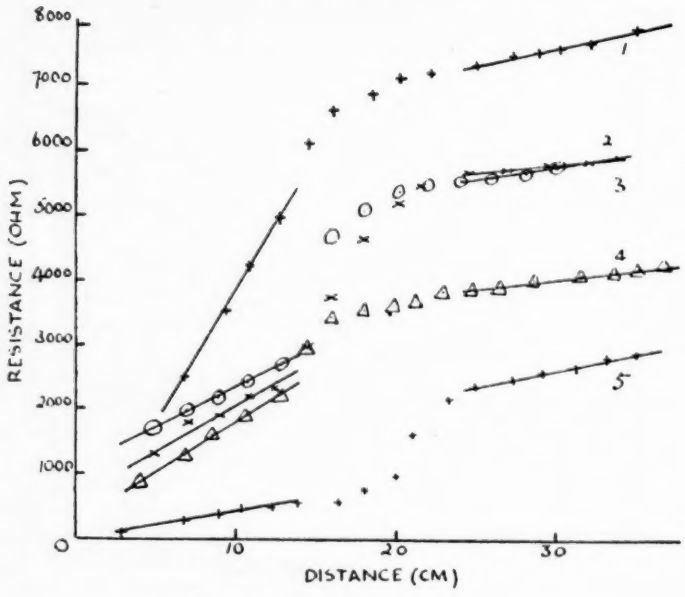


FIG. 6.—Effect of direction of milling.

together end to end; (4) when a number of such strips are molded together, no contact differences occur at the interfaces.

Other workers have also generally found anisotropic effects, but these experiments are different from those described elsewhere[5].

(*b*) *Effect of plying.*—The effects observed in the middle portions of the block just considered suggests that, in a block built from several plies, the resistivity would vary in the different plies. This may lead to odd results, in which case the number of plies should be kept to a minimum. Several experiments were designed to compare samples made from four strips cut from a sheet $\frac{1}{8}$ inch thick and samples made from two strips cut from a sheet $\frac{1}{4}$ inch thick. However, in all cases the results obtained from four-ply samples were so variable and unreliable that in all further experiments only two-ply samples were used.

(*c*) *Effect of milling and standing.*—In view of the importance of the dispersion of carbon black in the mechanism of conductivity, the time of milling may be expected to have some effect on the resistivity. To test this, four mixes of composition III were prepared in the laboratory, with milling times varying from 45 to 120 minutes. From each mix conductivity samples were prepared, some for immediate vulcanization and some for vulcanization after periods of 24 hours or 72 hours. After vulcanization at 280° F for 45 minutes, the samples were tested in the normal way.

The results showed that the resistivity increased with the length of time of standing in the unvulcanized state, but that the differences in the time of milling did not affect the resistivities of the samples. These results are shown in Table 4.

A second experiment was carried out which involved milling only. A batch of composition IV was given five minutes Banbury mixing and seven minutes

TABLE 4

EFFECT OF TIME OF MILLING AND STANDING

Resistivities in ohm-cm. and log resistivities

Time of milling (min.)	Vulcanized immediately		24 hours standing between milling and vulcanization		72 hours standing between milling and vulcanization	
	82		88		208	
		1.914		1.944		2.318
45	88		80		185	
		1.944		1.903		2.267
	146		142		232	
		2.164		2.152		2.365
60	214		121		210	
		2.330		2.083		2.322
	167		329		186	
		2.223		2.517		2.269
90	179		180		192	
		2.253		2.553		2.283
	176		163		201	
		2.246		2.212		2.303
120	121		176		160	
		2.083		2.246		2.204

on the laboratory mill. The sheet was then allowed to stand for 24 hours, after which two conductivity samples were cut out and vulcanized. The remainder of the sheet was milled for further periods of ten minutes, and at the end of each milling two further samples were prepared, making 12 in all.

One of these samples was defective, but the resistivities of the remainder are shown in Table 5. Although the mean resistivities do not vary with time of milling, the range of each pair decreases for longer milling times, suggesting improved dispersion.

TABLE 5

EFFECT OF TIME OF MILLING

Time (min.)	0	10	20	30	40	40 (After 7 days standing)
Resistivity (ohm-cm.)—						
First sample	14,050	8350	9700	7000	10,500	9380
Second sample	—	15,600	12,200	12,400	10,000	9150
Difference	—	6650	2500	5400	500	230

Time of Vulcanization.—Twelve samples were prepared from each of two different mixes (compositions IV and V) and pairs of samples from each mix were vulcanized at 280° F for 15, 30, 45, 60, 90 and 120 minutes, respectively. The results are shown in Table 6. The minimum resistivity for mix IV occurs after 90 minutes and for mix V after 60 minutes. The optimum vulcanizing times for tensile strength are, respectively, 90 minutes and 45 minutes.

Analysis of the variances of these results showed that the variation of resistivity with time of vulcanization is significant only when the 15-minute result is included. After 15 minutes the results show no significant variation among themselves, and it may be assumed that as long as a sample of either of these two compositions is vulcanized for at least 20 minutes, the exact time is not critical.

Reproducibility of results.—A series of mixes was prepared all of composition VI, but the rubber and black were chosen from different deliveries, so the compounds for the mixes fell into three groups between which batch differences

TABLE 6

EFFECT OF TIME OF VULCANIZATION

Mix IV						
Time of cure (min. at 280° F)	15	30	45	60	90	120
Resistivity (2 samples) (ohm-cm.)	503	253	256	170	162	224
	457	229	250	245	162	198
Mean	480	241	253	207	162	211
Mix V						
Time of cure (min. at 280° F)	15	30	45	60	90	120
Resistivity (2 samples) (ohm-cm.)	—	183	130	114	175	154
	1920	134	137	120	168	130
Mean	1920	158	134	117	172	142

were a maximum and within which they were a minimum, the materials in each group being, as far as possible, homogeneous. Mix A was prepared from the first group and mixed on Monday morning; three samples were vulcanized from this mix on Tuesday morning, and tested on Wednesday morning. B was taken from the first group, C and D from the second and E from the third group. Three samples were prepared from each mix as follows.

	Monday		Tuesday		Wednesday		Thursday		Friday
	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.	p.m.	a.m.
Mix	A	B	C	D	E	—	—	—	—
Cure	—	—	A	B	C	D	E	—	—
Test	—	—	—	—	A	B	C	D	E

The results are shown in Table 7 in ohm-cm. and also as logarithms of resistivity. Inspection shows that the variation between mixes greatly exceeds that between samples from the same mix. When the variances are analyzed statistically, no significant difference is found between the variations attributable to differences in source of ingredients and the variations due to mixing. The effects of these can therefore be pooled, giving, on the logarithmic scale, a standard deviation of 0.144 between mixes and 0.043 within mixes. No unusual variation is obtained by using different deliveries of black or rubber.

TABLE 7

REPRODUCIBILITY OF RESULTS USING ACETYLENE BLACK

Mix	Resistivities (ohm-cm.)			Mean	Logarithms			Mean
A	165	144	170	160	2.217	2.158	2.230	2.202
B	103	102	100	162	2.013	2.009	2.000	2.007
C	118	133	149	133	2.071	2.124	2.173	2.123
D	175	210	—	193	2.243	2.322	—	2.282
E	154	157	145	153	2.188	2.196	2.170	2.185

It is concluded from these results that resistivity measurements distinguish between mixes of different composition only when the difference in log resistivity exceeds about 0.3, *i.e.*, the larger resistivity must be more than double the smaller. Of course, discrimination can be made more exact by using more mixes of each composition.

At the conclusion of this experiment all the values for the resistivity of samples of composition VI which had been obtained in various other experiments were collected and averaged. The standard deviation of the log resistivities was 0.15, in close agreement with the figures obtained above.

In a further experiment, four mixes containing Dixie Voltex were prepared, A and B of composition IV and C and D of composition V. Two samples of each were vulcanized at 280° F, mix IV for 45 minutes and mix V for 90 minutes. The vulcanized samples were tested in the usual way, and the results are shown in Table 8. Inspection shows that here again variations between mixes exceed those within mixes. The variances were analyzed as before, and it was found that there was no significant difference in the values from mixes of the two compositions. The results for both compositions were therefore pooled, giving, on the logarithmic scale, a standard deviation of 0.137 between mixes and 0.059 within mixes.

TABLE 8

REPRODUCIBILITY USING DIXIE VOLTEX

Mix	Resistivity (ohm-cm.)		Mean	Logarithm		Mean
A (IV)	313	285	299	2.496	2.455	2.476
B (IV)	252	281	267	2.401	2.449	2.425
C (V)	366	446	406	2.563	2.649	2.606
D (V)	278	206	242	2.444	2.319	2.382

Comparing these results gives 0.144 between mixes and 0.043 within mixes for acetylene black and 0.137 between mixes and 0.059 within mixes for Dixie Voltex. These agree closely, and the mean of 0.14 between mixes and 0.05 within mixes represents a significant difference at the 0.1 per cent level.

THE DEVELOPMENT OF HIGHLY CONDUCTING RUBBER

It is not a difficult matter to prepare in the laboratory compounds with relatively high conductivity and, as mentioned above, a compound with specific resistance as low as 1 ohm-cm. has been reported. These highly conducting compounds are, however, difficult to process under normal production conditions. It was, therefore, decided to find to what extent the specific resistance of rubber can be reduced, while still retaining the ability to be processed. The processing tests to which the compounds were subjected involved mixing 25-lb. batches on a 40-inch mill, and calendering to a thickness of about 0.02 inch on an 84-inch three-bowl calender.

Four compounds were mixed in the laboratory with acetylene black content increasing up to 80 parts of black on 100 parts of rubber. The compositions of the compounds are given in Table 9, which also contains the values of the specific resistance. Each of the latter is the mean of the results from duplicate tests.

TABLE 9

	VII	VIII	IX	X
Smoked sheet rubber	100	100	100	100
Acetylene black	20	40	60	80
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Pine tar oil	3	3	3	3
Mercaptobenzothiazole	0.8	0.8	0.8	0.8
Sulfur	2	2	2	2
Resistivity (ohm-cm.)	65×10^7	174	74	13.2

Compound IX was processed satisfactorily but it was found that the power available to drive the factory mixing mill was insufficient to enable compound X to be mixed. The driving motor stalled before all the black had been added.

The next step was to mix in the laboratory a series of compounds with varying acetylene black and softener loadings. The accelerator was changed from mercaptobenzothiazole to benzothiazoyl disulfide to reduce the tendency for scorching. The compositions and specific resistances are given in Table 10.

TABLE 10

	XI	XII	XIII	XIV	XV	XVI	XVII	XVIII
Smoked sheet rubber	100	100	100	100	100	100	100	100
Acetylene black	80	80	80	80	100	100	120	120
Pine tar oil	3	10	15	20	20	30	40	50
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2
Benzothiazoyl disulfide	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulfur	2	2	2	2	2	2	2	2
Resistivity (ohm cm.)	24	19.8	13.3	4.8	10.0	8.4	3.7	7.1

Compound XIII was processed satisfactorily, and two lots of sheeting were made from two batches mixed at different times. The sheeting was wrapped on a hollow drum and vulcanized in open steam for 1 hour at 280° F after a half-hour rise. The specific resistance of a number of samples taken from different parts of the sheets was determined. The average for the first sheet was 25.9 ohm-cm. and for the second 13.5 ohm-cm. These values provided further evidence that considerable variation in electrical properties is possible for a particular compound mixed and processed at different times.

To find the order of this variation, samples of compound XIII were made in a number of different ways. Batches were mixed and conductivity samples vulcanized in the laboratory on three different occasions by different operators and also similar samples were vulcanized using material that had been mixed on the 40-inch mill, with and without subsequent calendering. In all, seven different methods of preparation were employed and 18 samples tested, including the two 0.02-inch sheets. The mean of all tests was 15.7 ohm-cm., with a standard deviation of 5.6.

A thin calendered sheet was also prepared from compound XVIII, but its preparation was rather more difficult than for compound XIII. The mean specific resistance for the sheet was 13 ohm-cm. It seems probable that this compound could be processed to give sheets with lower specific resistance than XIII, but more tests would be needed to establish this with certainty.

ANTISTATIC TIRES

Effects of static electricity.—For some time past, workers in the rubber industry have been considering the question of the generation of static electricity in road vehicles[8]. This problem arose particularly in connection with the interference in car radios by discharges of static electricity. Various solutions to the problem have been attempted, such as pumping graphite into inner tubes[9] or coating the inner plies of the carcass with an aqueous suspension of graphite. However, the most promising results are obtained with conducting rubber, either in the side wall to bring the charge on the vehicle close to the ground and so reduce its potential or in the tread to conduct to earth charges as produced.

In the last few years, various omnibus companies have reported almost daily cases of persons suffering severe electric shocks when mounting or dismounting gasoline-driven buses, the voltages encountered being estimated at from 5000–50,000 volts. This led to an intensification of research mainly directed towards producing bus tires that would be electrically conducting and yet as hard wearing and reliable as ordinary tires.

The mechanism of generation.—As a rubber pneumatic tire rolls over any surface, equal and opposite charges are produced, either by friction or by contact between the tire tread and the road surface. The exact difference between the mechanisms of separation and friction is not known and they may be variations of the same process.

As the wheel revolves, work is done in separating the charges, and so a high potential difference is produced between them. The negative charge on the tire tread induces a positive charge on neighboring parts of the vehicle, *e.g.*, the mudguards, leaving a free negative charge at high potential on the body of the vehicle (Figure 7). As the distance of the charge from the point of contact increases, its tendency to leak away increases, and the charge builds up until the leakage by atmospheric conduction, by conduction through the rim and tire and by other means, balances the production of charge. Equilibrium is eventually set up between the distributed charge around the tire tread, which may be considered equivalent to a definite charge at a definite potential at a definite point A, and the various charges on the road and on the vehicle.

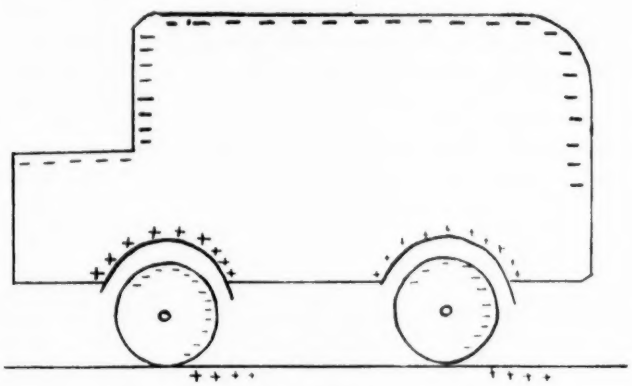


FIG. 7.—Distribution of static charges on a vehicle.

Detection and measurement of static charges.—Various experiments are described in the literature, and from these and other experiments it is found that (1) static charges are produced only on moving vehicles, irrespective of whether or not the engine is running; this means the charges are produced by the tires and not by the engine or exhaust; (2) no effects are produced on wet roads or with wet tires, although a humid atmosphere alone does not prevent the build-up of static charges; (3) certain road surfaces are more efficient in giving rise to static charges than others.

In one experiment, a spark gap was fitted to a heavy vehicle, with a chain trailing from one electrode to the ground. The voltage across the spark gap was measured by means of a voltmeter consisting of a sensitive galvanometer in series with a high resistance. The significant fact was discovered that the

galvanometer deflection was independent of the series resistance used. That is, the current leaking from the vehicle is fundamental but the voltage built up is not.

Consideration of the mechanism of generation leads to the same conclusion. It would seem that the rate of charge build-up is fixed, and equilibrium is reached when the current in amperes flowing through the various leakages is equal to this rate of charge build-up in coulombs per second. In these circumstances the voltage of the vehicle is the product of the current in amperes through the leakage and the resistance in ohms of the leakage.

The preliminary measurement with a galvanometer showed that when this was connected direct across the spark gap or in series with a resistance less than 100 megohms a current of about 30 microamperes flowed. This corresponds to a rate of build-up of charge of 90,000 electrostatic units per second.

A later development was the use of a valve electrometer, described by Bulgin[10]. This instrument is housed in a steel tube which is directed at a charged surface, when the potential can be calculated from the reading of an attached dial if the distance of the surface from the instrument is known.

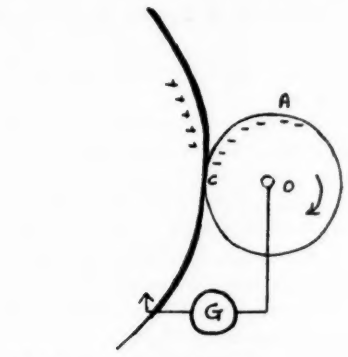
An experimenter riding on a lorry or a bus can direct the electrometer at the ground and so measure the potential of the vehicle to earth while travelling. Alternatively, the experimenter can stand on the ground and direct the electrometer at the vehicle while it is stopping or starting. In this way a considerable amount of information may be collected.

Experimental methods.—Experiments showed that when tires with the treads made in conducting rubber were fitted to lorries and other vehicles these ran at a lower potential than when fitted with standard tires, and as a result of several exhaustive experiments using the valve electrometer, a body of data was obtained. The range of voltages recorded did not include values as high as some of those quoted in the literature, *e.g.*, 50,000 volts. However, it is not known under what conditions such values were obtained, and it is probable that in these cases the resistances of the tires were unusually high. From these data it was decided that more detailed experiments could most conveniently be done by running the tires on a test wheel, and a series of experiments was designed.

The rig was of National Bureau of Standards design, with the wheel against which the tire runs insulated from the rim on which the tire is mounted. The steel axle of the rim was connected in series with a switch, a microammeter, and the framework carrying the steel driving wheel. The circuit was completed through this wheel and the test tire as shown in Figure 8. In the equivalent circuit, also shown in Figure 8, R_O is the direct resistance through and along the tread from A to C, R_T is the resistance between the tread and the center of the rim, R_M is the resistance of the rig from one wheel to the other (which exceeds 10^{10} ohms) and R_G is the resistance of the galvanometer and the connections between O and C. As R_M is very large compared with R_T, it may be regarded as infinite. R_G on the other hand is so small compared with R_T that it may be neglected, and is not considered in the following discussion.

In the tests the tire was driven at speeds of 13, 18 and 30 miles per hour. While the tire was rotating at a steady speed, the highest voltage on the tread was measured. The highest voltage occurred at the highest point of the tire, *i.e.*, 90° from the point of contact. A second reading of the tread voltage was taken when the circuit was broken by means of the switch.

Interpretation of results.—The charges distributed around the tread of the



WHEEL ON TEST RIG

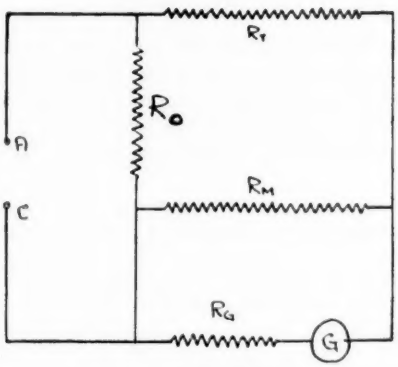


FIG. 8.—Equivalent circuit.

tire may be regarded as equivalent to a definite charge, Q, concentrated at a point A, and this charge may be regarded as at a potential V (Figure 8).

The electrometer was used to measure the various voltages around the tread, the maximum values on short circuit (V_1) and open circuit (V_2) being recorded. It is assumed that V is proportional to V_1 and V_2. The various leakage resistances may be regarded as equivalent to a resistance R_1 between A and C through O and a resistance R_2 along the tread from A to C (equal to R_O in Figure 8). If the current through R_1 is i and through R_2 is $(I - i)$ the total current is I. In equilibrium, $I + (dQ/dt) = O$.

If, as believed, dQ/dt is constant for a given speed then I should be constant when the tire is running:

$$V = R_2(I - i) = R_1 i$$

on open circuit $KV = V_2$, $i = O$ and R_1 is infinite:

$$\therefore \quad V_2 = KR_2I \tag{1}$$

on short circuit $KV = V_1$ and $R_1 = R_T$:

$$\therefore \quad V_1 = KR_2(I - i) = KR_1 i \tag{2}$$

i is the current through the galvanometer.

From Equations (1) and (2) I, KR_1 and KR_2 can be calculated from i, V_1 and V_2.

Tests on tires.—Eleven 9.00 × 20 tires were run on the test wheel and their conducting properties compared.

Nos. 1, 2 and 3 were new tires of standard construction. No. 4 was a standard tire worn uneven. No. 5 was a standard tire worn completely smooth and was tested when it was warm from running as well as cold when starting. Nos. 6, 7 and 8 were built with normal carcasses but with tread and side walls in conducting rubber of compositions XIX, XX and XXI respectively. No. 7A was identical with No. 7. No. 9 was identical with No. 8, but part of the side wall was cut away so that there was no connection between the tread and the bead except through the carcass. No. 10 was built with a normal carcass and tread but with highly conducting sidewalls.

The readings obtained on the microammeter were steady, and were probably accurate to ±2 microamperes. The voltage readings however were subject to considerable error for the following reasons.

(1) The tire is not a plane surface and not large enough to subtend an angle of 90° at the mouth of the tube, which is the condition for accurate determinations. This means that readings are less than the true value.

(2) To reduce the error due to (1), the tube was held closer to the tire, but this increased the percentage error in the distance. The actual distance was about 6 ± 1 inches.

(3) Voltages of over 1000 could not be read when the instrument was so close, and so the error due to (1) was greater for high voltages than for low ones.

However, by reasonable care results were obtained which are thought to be within 50 per cent of the correct figures.

The results for the eleven tires are shown in Table II.

Results of tire tests.—The values of V_1, V_2 and i have been recorded, and those for KR_1, KR_2 and I calculated. The values for I have been converted into electrostatic units per second. The values of I at 30 m.p.h. are 24, 141, 109, 60, 18, 90, 75, 87, 30 and 112 × 10^3 electrostatic units per second. These are remarkably close, the limits being 18 and 141 (×10^3 electrostatic units) compared with limits of 0 and 3500 in the voltages, and the trend of the values is in no way systematic. It seems probable then that the hypothesis that the rate of production of charge is constant at constant speed, irrespective of the composition of the tread rubber, is true and that the variations are due to experimental errors. The mean values of I (in thousands of electrostatic units per second) are 33 ± 10 at 13 miles per hour, 45 ± 15 at 18 miles per hour, and 75 ± 28 at 30 miles per hour.

Assuming that the value of I was the same for all tires at the same speed and that R_1 and R_2 were constant for all speeds on the same tire, the expected values of V_1, V_2 and i can be calculated, and are shown in brackets. It will be seen that the differences between the actual values and the theoretical values for V_1, V_2 and i are within the limits of experimental error. Hence this experiment confirms that the rate of production of charge is approximately constant for all tires at the same speed and is about 75,000 electrostatic units per second at 30 miles per hour.

From Table 11 it will be seen that the tread and leakage resistances of the standard tires are all of the same order, but that the tread resistance is less in the case of the worn tires. This may be attributed to better contact with the

TABLE II

RESULTS OF RIG TESTS ON ELEVEN SELECTED TIRES

Tire No.	Description	Speed (m.p.h.)	Voltage V_1 (volts)	Voltage V_2 (volts)	Current i (microamp.)	Resistance KR_1 (megohms)	Resistance KR_2 (megohms)	Current I 10^5 e.s.u. per second
1	Standard	13	500 (700)	1500 (920)	2.8 (2.6)	178 (266)	357 (84)	13 (33)
		18	600 (950)	2000 (1250)	3.8 (3.6)	158 (266)	368 (84)	17 (45)
		30	1000 (1600)	3000 (2100)	5.4 (6.0)	185 (266)	371 (84)	24 (75)
2	Standard	13	750 (720)	1500 (2000)	8.0 (7.0)	94 (103)	94 (180)	48 (33)
		18	1000 (1000)	2000 (2700)	10.0 (9.5)	100 (103)	100 (180)	64 (45)
		30	2500 (1700)	3500 (4500)	13.5 (16.0)	185 (103)	74 (180)	141 (75)
3	Standard	13	700 (360)	1500 (2100)	10.2 (9.1)	69 (40)	78 (194)	55 (33)
		18	750 (500)	2000 (2900)	12.9 (12.4)	58 (40)	97 (194)	62 (45)
		30	1250 (830)	2500 (4800)	18.2 (20.7)	69 (40)	69 (194)	109 (75)
4	Standard (worn uneven)	13	550 (435)	750 (550)	3.3 (2.5)	167 (170)	61 (50)	37 (33)
		18	500 (580)	950 (750)	3.0 (3.4)	167 (170)	150 (50)	20 (45)
		30	750 (1000)	1000 (1250)	5.0 (5.7)	150 (170)	50 (50)	60 (75)
5	Standard (worn smooth), cool	13	400 (280)	550 (300)	1.6 (0.9)	250 (297)	94 (28)	18 (33)
		18	400 (380)	500 (400)	1.4 (1.3)	286 (297)	71 (28)	21 (45)
		30	500 (630)	650 (700)	1.4 (2.1)	357 (297)	108 (28)	18 (75)
5	Standard (worn smooth), warm	13	600 (430)	1000 (660)	5.0 (3.8)	120 (113)	80 (60)	38 (33)
		18	650 (590)	650 (900)	5.7 (5.2)	114 (113)	0 (60)	(45)
		30	1500 (1000)	1500 (1500)	6.5 (8.7)	230 (113)	0 (60)	(75)

* Voltages too small to read. † Current too small to read.

TABLE II—*Continued*

Tire No.	Description	Speed (m.p.h.)	Voltage V_1 (volts)	Voltage V_2 (volts)	Current i (microamp.)	Resistance KR_1 (megohms)	Resistance KR_2 (megohms)	Current I 10^3 e.s.u. per second
6	Conducting	13	5 (4)	10 (7)	6.5 (4.7)	0.77 (0.85)	0.77 (0.64)	39 (33)
		18	5 (6)	10 (10)	9.2 (6.4)	0.54 (0.85)	0.54 (0.64)	54 (45)
		30	10 (9)	15 (16)	10.0 (10.7)	1.00 (0.85)	0.50 (0.64)	90 (75)
7	Conducting	13	30 (28)	75 (64)	5.0 (6.3)	6.0 (4.4)	9.0 (5.8)	25 (33)
		18	45 (37)	90 (87)	10.0 (8.5)	4.5 (4.4)	4.5 (5.8)	60 (45)
		30	55 (63)	150 (145)	16.0 (4.2)	3.4 (4.4)	5.9 (5.8)	75 (75)
7A	Conducting	13	25 (25)	60 (66)	4.5 (6.5)	5.5 (4.0)	7.8 (6.0)	23 (33)
		18	40 (40)	110 (90)	12.0 (9.0)	3.3 (4.0)	5.8 (6.0)	57 (45)
		30	60 (60)	175 (150)	19.0 (15.0)	3.2 (4.0)	6.1 (6.0)	87 (75)
8	Conducting	13	5 (5)	10 (7)	3.0 (2.5)	1.7 (2.0)	1.7 (0.6)	18 (33)
		18	5 (7)	10 (9)	4.2 (3.4)	1.2 (2.0)	1.2 (0.6)	25 (45)
		30	10 (11)	15 (15)	4.3 (5.7)	2.3 (2.0)	1.2 (0.6)	39 (75)
9	Conducting (sidewalls cut)	13	* (7)	* (7)	† (0.01)	— (500)	— (0.6)	— (33)
		18	* (9)	* (9)	† (0.02)	— (500)	— (0.6)	— (45)
		30	* (15)	* (15)	† (0.03)	— (500)	— (0.6)	— (75)
10	Standard tread conducting sidewalls	13	40 (20)	1000 (650)	16 (12)	2.5 (2.1)	60 (58)	50 (33)
		18	50 (30)	1500 (850)	22 (15)	2.3 (2.1)	66 (58)	68 (45)
		30	55 (40)	1750 (1450)	36 (34)	1.5 (2.1)	47 (58)	112 (75)

* Voltages too small to read. † Current too small to read.

wheel. The various conducting tires give lower resistances than the standard tires, both for the tread and the leakage. Tire No. 10 made with conducting sidewalls and a standard tread gives a tread resistance similar to the standard tires and a leakage resistance comparable with the conducting tires. All these results are to be expected, and hold true whether the observed results or the theoretical results are considered.

In the case of the tire with the cut-away sidewalls, the voltages were of the same order as the variable zero error (about 10–20 volts), and so could not be measured. No current was recorded by the microammeter. Assuming that the tread resistance was the same as tire No. 8 (viz., 600,000 ohms) and that the carcass resistance was twice that of a standard tire (*i.e.*, about 500 megohms), the expected voltage and current could be calculated. The voltage is below 15 and the current is 0.02 microamperes, well below the range of the instrument. Therefore the results found for this tire also fit in with the general theory.

Application of theory.—As $V_2 = KR_2I$ and I is known for all tires, then if the equivalent potential of a tire at 30 miles per hour is V volts, V = resistance of tread in ohms $\times 25 \times 10^{-6}$.

TABLE 12

COMPARISON OF RESISTANCE FIGURES

Tire	Rim-to-earth resistance R (ohm)	Leakage resistance KR_1 (ohm)	Tread resistance KR_2 (ohm)	Specific resistance R_s (ohm-cm.)	$\frac{KR_2}{R_s}$
No. 2, standard	3×10^8	1.0×10^8	1.8×10^8	1.1×10^6	164
No. 3, standard	3×10^8	4.0×10^7	1.9×10^8	1.1×10^6	173
No. 6, conducting	—	8.5×10^5	6.4×10^5	6.3×10^3	101
No. 7, conducting	—	4.4×10^6	5.8×10^6	3.0×10^4	193
No. 8, conducting	1×10^6	2.0×10^6	6.0×10^5	4.7×10^3	128
No. 9, cut sidewalls	1×10^8	5.0×10^8	6.0×10^5	4.7×10^3	128

$$\text{Mean ratio } \frac{KR_2}{R_S} = 148\text{:S.D.} = 34.$$

In Table 12, values of KR_1 and KR_2 are compared with the total rim-to-earth resistance measured by inserting a battery in the circuit shown in Figure 8 and recording the voltage and current while the tire is stationary. Values of the specific resistance are also compared, and it is seen that the ratio $KR_2/R_S = (1.5 \pm 0.2) \times 10^2$.

It follows that:

$$KV = (25 \pm 9) \times 10^{-4} \times (1.5 \pm 0.2) \times R_S = (39 \pm 18) \times 10^{-4} \times R_S$$

It is found that the average value of KV for a tire of standard construction on the test rig is 3000, whereas the average potential of a doubledecker bus shod with the same tires and running at 30 miles per hour is 1000 volts. It seems reasonable to assume, therefore, that the potential of a bus running on six tires whose treads have a specific resistance of R_S ohm-cm. will be of the order of $(13 \pm 6) \times 10^{-4} \times R_S$ volts. Hence, to produce satisfactory tires, it is necessary to know the maximum permissible potential, from which can be calculated the maximum resistivity. Compounds for use in treads can then be tested in the laboratory for suitability by measuring their resistivity.

This formula can be applied to the six tires from the last experiment for which the tread resistivity is known, and in Table 13 the actual voltages ob-

tained on the rig are compared with the voltages calculated from the specific resistance. The ratios have been worked out, and the mean value is 1.2, with a standard deviation of 0.3, representing good agreement.

These results can also be applied to the case quoted of the vehicle for which the estimated leakage current was 9×10^4 electrostatic units per second. According to Table II the leakage and tread resistances are approximately equal, so the current in each is probably the same. This would make the total charge generated 18×10^4 electrostatic units per second equivalent to 3×10^4 electrostatic units per second for each tire at a speed of 15–20 miles per hour. This compares with 4.5×10^4 electrostatic units per second for a single tire on the test rig at a speed of 18 miles per hour.

TABLE 13

ESTIMATION OF VOLTAGE ON TIRES FROM FORMULA

Tire No.	Actual voltage	Calculated voltage	Ratio
2	3500	4200	1.20
3	2500	4200	1.68
6	15	24	1.60
7	150	115	0.77
8	15	18	1.20
9	approx. 15	18	1.20

Mean ratio = 1.2:S.D. = 0.3.

Summary and conclusion.—In the first part of this paper a method is described for measuring the resistivity of rubber compounds with reasonable accuracy and reproducibility, and it is shown how this property is affected by various factors.

In the second part it is shown how the ability to make such measurements was instrumental in developing highly conducting rubbers, and a compound is described (with a resistivity of 10 ohm-cm.) which can be processed under normal factory conditions.

In the last part of the paper, the generation of static electricity by tired vehicles is discussed, and a theory evolved whereby the effects to be expected on a vehicle can be predicted, from laboratory tests of the sort described in the first part of the paper, to within about 50 per cent of the true value. It has been suggested that tires capable of reducing the effects of static electricity to any desired degree can be developed largely by means of these laboratory tests.

ACKNOWLEDGMENT

Acknowledgment is made to the Directors of the Avon India Rubber Co., Ltd., for permission to publish the results contained in this paper.

REFERENCES

[1] Dawson and Porritt, "Rubber: Physical and Chemical Properties", Research Assocn. of Brit. Rubber Manufrs., Croydon, **1935**; Kemp and Hermann, *Proc. Rubber Tech. Conf. London*, **1938**, p. 893.
[2] Elden, *Rubber Age* (N.Y.) **47**, 308 (1944).
[3] Kemp and Hermann, *Proc. Rubber Tech. Conf. London*, 1938, p. 893.
[4] Sweitzer and Goodrich, *Rubber Age* (N.Y.) **55**, 469 (1944); Bulgin, *Trans. Inst. Rubber Ind.* **21**, 188 (1945).
[5] Newton, *J. Rubber Research* **15**, 35 (1946).
[6] Bulgin, *Trans. Inst. Rubber Ind.* **21**, 188 (1945).
[7] Bulgin, *Trans. Inst. Rubber Ind.* **21**, 188 (1945); Wack, Anthony, and Guth, *J. Applied Physics* **18**, 456 (1947).
[8] Cadwell, Handel and Benson, *Am. Chem. Soc. News Ed.* **19**, 1139 (1941); Beach, *Elec. Eng.* **60**, 202 (1941); Liska and Hanson, *Ind. Eng. Chem.* **34**, 618 (1942); Makeown and Vouk, *Trans. Am. Inst. Elec. Eng.* **62**, 207 (1943); Woods, *Distribution of Electricity* **17**, 57.
[9] Cadwell, Handel and Benson, *Am. Chem. Soc. News Ed.* **19**, 1139 (1941).
[10] Bulgin, *J. Scientific Instruments* **22**, 188 (1945).

STABILITY OF ACCELERATORS AS AFFECTED BY HIGH PROCESSING TEMPERATURES *

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High-speed processing of rubber compounds appears to be gaining widespread acceptance in the rubber industry. In general, this is typified by compounding in Banbury mixers operating at 40 r.p.m. Such drastic working naturally develops high stock temperatures, which may easily reach the level of 360° F.

From an economic standpoint, it is desirable to introduce the accelerators into the Banbury during the latter part of the mixing cycle. In certain instances where this has been done, there have been reports from the field of a loss in accelerator activity. In view of this, a study was undertaken to determine what, if any, might be the adverse effects of processing temperatures of the order of 360° F on the stability of representative and commonly used accelerators.

A total of twenty-two accelerators or accelerator combinations were examined. These were picked to include the more widely used representatives of the five major accelerator classifications, namely thiazoles, thiurams, dithiocarbamates, guanidines, and aldehydeamines.

PROCEDURE

The testing was done with natural rubber compounds and for the most part with a typical tread type stock. In the case of certain of the aldehydeamines a nonblack mix was used because of the known retarding action of channel black on these particular materials. The recipes were as follow.

Test Recipes

Tread type		Nonblack	
Smoked sheet rubber	100.0	Smoked sheet rubber	100.0
Zinc oxide	5.0	Zinc oxide	5.0
MPC black	45.0	Whiting	50.0
Fatty acid	3.5	Fatty acid	0.5
Pine tar	3.5	Light process oil	3.0
Antioxidant	1.0	Antioxidant	1.0
Sulfur	3.0	Sulfur	3.0
Accelerator	as desired	Accelerator	as desired

Mixing was carried out in a size-B laboratory Banbury operating at 116 r.p.m., and with enough steam in the jacket to develop a stock temperature of 360° ± 5° F, determined by a needle pyrometer thrust into the batch immediately after discharge.

Each accelerator or combination was added to duplicate batches having

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identical formulas and mixing cycles, but with differences in time and manner of accelerator addition (Figure 1). In the one instance, the accelerator was introduced into the Banbury two minutes before completion of the mix and thus subjected to the high temperatures generated (360° F). In the second instance, addition was after the Banbury operation and while the batch was being worked on a 6 × 12-inch sheeting mill with roll temperatures of 150° F. It was felt that, under these latter conditions, batch temperatures would be insufficient to cause impairment of accelerator activity and in the case of each material, performance could be considered as standard.

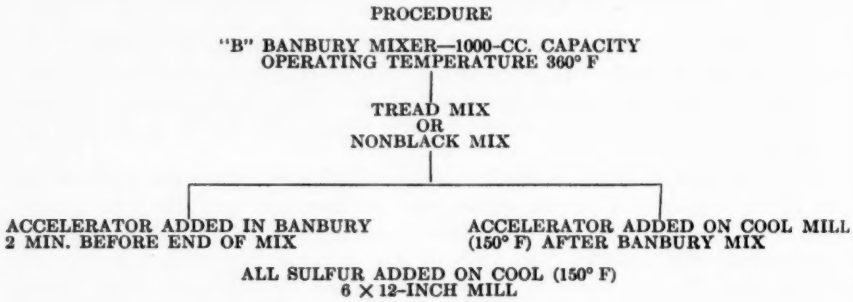

FIG. 1.

Change in accelerator activity as affected by processing temperatures was based on differences in physical properties after vulcanization which were found to exist between a standard batch and that in which the same accelerator was added during the high-temperature Banbury mixing.

Specifically, A.S.T.M. test-slabs of each stock, cured for 30, 45, 60 and 75 minutes at 274° F, respectively, were prepared. The average tensile strength, 300 per cent modulus, breaking elongation, and T-50 values for all four cures on any one stock were determined. The results have been expressed as percentage retained or average change in property as between standard and "hot" Banbury accelerator addition. Indications of impairment of accelerator activity are a drop in the level of tensile strength and modulus values, and positive average change in T-50 and breaking elongations. Modulus was judged to be the most sensitive indicator.

PROCESSING TEMPERATURE *VS.* ACCELERATOR ACTIVITY

Thiazoles and thiazole derivatives.—In this group, based on the behavior of the representative members chosen, any impairment in accelerating strength from processing at 360° F is considered slight. It is, therefore, concluded that this class of accelerators may be used safely under such conditions. It is to be noted that the *N*-cyclohexylbenzothiazyl sulfenamide did appear to have somewhat less stability than the other accelerators tested. The results are shown in Table I.

Activated thiazoles.—In this group, in which a thiazole is used as the primary accelerator, it is seen that slightly more impairment resulted from the high temperature processing than in the case of the thiazole alone. To some extent this may be due to impairment of the secondary accelerator. The group is considered generally suitable for use in high temperature processing. The results are shown in Table II.

TABLE I

COMPARATIVE STABILITY OF THIAZOLES IN A TREAD STOCK

(Banbury Processed at 360° F)

Accelerator	Amt.	Retained		Average change	
		Tensile	Modulus	T-50	Elong.
2-Mercaptobenzothiazole	1.0	101.5%	94%	+3.0° C	+3.0%
Benzothiazyl disulfide	1.0	103.0	92.8	−0.9	+6.0
Phenylaminomethylbenzothiazyl sulfide	1.0	104.6	93.8	+3.1	+4.0
N-Cyclohexylbenzothiazyl sulfenamide	0.5	97.0	77.0	+2.5	+7.0

TABLE II

COMPARATIVE STABILITY OF ACTIVATED THIAZOLES IN A TREAD STOCK

(Banbury Processed at 360° F)

Accelerator	Amt.	Retained		Average change	
		Tensile	Modulus	T-50	Elongation
Benzothiazoyl disulfide Diphenylguanidine	0.5 0.25	105.7%	88.0%	+4.8° C	+ 4.2%
Benzothiazoyl disulfide Tetramethylthiuram monosulfide	0.625 0.0625	106.2	84.5	+4.0	+ 8.0
Benzothiazoyl disulfide Diphenylguanidine phthalate	0.5 0.35	97.2	86.2	+4.1	+11.0
2-Mercaptobenzothiazole *N*-Nitrosodiphenylamine	1.0 0.5	90.0	93.5	+4.2	+ 5.0
N-Cyclohexylbenzothiazyl sulfenamide Bis-*N*,*N*′ (2 benzothiazylthiomethyl) urea	0.25 0.35	94.0	86.7	+3.5	+ 2.0

Dithiocarbamates.—With the dithiocarbamates the effects of high temperature (360° F) processing are damaging. It is of interest to note that the extent of the damage varies inversely with the chain length of the alkyl radicals on the nitrogen atom in the molecule. Thus zinc dimethyldithiocarbamate and benzal-bis-dimethyldithiocarbamate show nearly 60 per cent loss in both tensile strength and modulus, while for the zinc diethyl and selenium diethyl compounds the loss is only 35 to 40 per cent. Proceeding to the zinc dibutyldithiocarbamate, it is found to be affected less than 10 per cent. The results are shown in Table III.

Thiurams.—Heavy damage also occurs in this group at processing temperatures of 360° F. This would be expected from the close chemical relationship to the dithiocarbamates. Likewise, the tolerance of high temperature seems to improve from the mono- to the disulfide or with an increase in weight in the alkyl substitution on the nitrogen atoms in the molecule. Thus, tetramethylthiuram monosulfide was found to lose significantly more of its accelerating value than the tetramethylthiuram disulfide, while the tetraethylthiuram disulfide loses still less. None of these three accelerators appears to fall within the range considered satisfactory for high-temperature processing. Results are shown in Table IV.

TABLE III

COMPARATIVE STABILITY OF DITHIOCARBAMATES IN A TREAD STOCK

(Banbury Processed at 360° F)

Accelerator	Amt.	Retained		Average change	
		Tensile	Modulus	T-50	Elongation
Zinc dimethyldithiocarbamate	0.2	44.0%	39.5%	+19.4° C	+11.0%
Zinc diethyldithiocarbamate	0.2	71.8	68.8	+19.9	+ 5.0
Zinc dibutyldithiocarbamate	0.3	95.6	90.5	+ 5.9	+ 2.0
Selenium diethyldithiocarbamate	0.2	64.0	60.8	+18.0	+ 7.0
Benzal-bis-dimethyldithiocarbamate	0.3	44.5	41.3	+26.8	+ 9.0

TABLE IV

COMPARATIVE STABILITY OF THIURAMS IN A TREAD STOCK

(Banbury Processed at 360° F)

Accelerator	Amt.	Retained		Average change	
		Tensile	Modulus	T-50	Elongation
Tetramethylthiuram monosulfide	0.2	65.3%	39.8%	+24.7° C	+11.0%
Tetramethylthiuram disulfide	0.2	78.4	55.5	+20.8	+ 7.0
Tetraethylthiuram disulfide	0.3	85.4	72.6	+20.0	+ 2.0

Although the loss of accelerating strength is probably a function of both time and temperature, for practical purposes it may be considered as dependent on temperature only. No significant improvement in retention of properties of the tetramethylthiuram monosulfide compound resulted by reducing the time of exposure to the high temperature in the Banbury from two minutes to one minute. A substantial improvement was obtained, however, by reducing the mixing temperature from 360° to 300° F. Probably the safe upper limit for processing the thiurams is in the neighborhood of 275° F.

Miscellaneous amine accelerators.—This group consisted only of butyraldehydeaniline and diphenylguanidine. In a tread stock, both these dissimilar accelerators were classified as intermediate with respect to stability during high-temperature processing. This suggests that the best application is that of activators for more stable accelerators. Results are to be found in Table V.

TABLE V

COMPARATIVE STABILITY OF MISCELLANEOUS AMINE ACCELERATORS IN A TREAD STOCK

(Banbury Processed at 360° F)

Accelerator	Amt.	Retained		Average change	
		Tensile	Modulus	T-50	Elongation
Butyraldehydeaniline	1.0	83.8%	74.0%	+3.0° C	+4.0%
Diphenylguanidine	1.75	93.5	78.4	+5.2	+1.0

Aldehydeamines.—As mentioned previously, the aldehydeamines studied were compared in a nonblack stock because of the known retarding action of channel black on some of them. None of the three tried showed significant loss in activity when processed at 360° F. Butyraldehydeaniline was found to be the most tolerant of high temperature. Both heptaldehydeaniline and triethyltrimethylene triamine, though affected somewhat more, are considered to have satisfactory stability. Results are in Table VI.

TABLE VI
COMPARATIVE STABILITY OF ALDEHYDEAMINES IN A NONBLACK STOCK

(Banbury Processed at 360° F)

Accelerator	Amt.	Retained		Average change	
		Tensile	Modulus	T-50	Elongation
Butyraldehydeaniline	0.75	100.2%	100.5%	+1.0° C	+2.0%
Heptaldehydeaniline	0.35	90.1	90.2	+3.4	+8.0
Triethyltrimethylene triamine	1.0	100.2	93.8	+0.8	+4.0

SUMMARY

In high-speed Banbury mixing, sufficiently high temperatures may be generated at least to partially damage some rubber accelerators and decrease their effective activity. Thus, at a processing temperature of 360° F, the following stability relationships hold.

1. Thiazoles, thiazole derivatives, and activated thiazoles show little loss of activity.
2. Thiurams and dithiocarbamates may be severely affected.
3. Guanidines, as represented by diphenylguanidine, are only moderately affected.
4. Aldehydeamines range in stability from moderate to good.

This effect of high temperature on accelerator stability may be considered as constituting a processing hazard.

The proper selection of accelerators and the careful consideration of any processing changes which may significantly increase temperature minimize the danger and allow avoidance of harmful results.

The fact that some accelerators are relatively unstable at high temperatures does not preclude their use. It is simply necessary to incorporate these materials into the mix at a sufficiently low temperature, such as that at which it is normally considered safe to add sulfur.

BIBLIOGRAPHY

Wiegand, "Effect of Overmilling on Compounded Rubber", RUBBER CHEM. TECH **5**, 671 (1932).
Lefcaditis, "Studies in the Interfacial Relationships between Rubber and Fillers. IV. The Effect of Mastication on the Properties of Vulcanized Rubber", RUBBER CHEM. TECH. **6**, 475 (1933).

BASIC REACTIONS OCCURRING DURING RUBBER RECLAIMING. II. THE INFLUENCE OF SOLVENT NAPHTHA, STORAGE OF RECLAIM AND AGING OF SCRAP PRIOR TO RECLAIMING, AND INFRARED SPECTRA OF NATURAL RUBBER RECLAIM *

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A previous investigation[1] of the reactions which occur during various periods of time of rubber reclaiming in the presence of solutions of defibering agents or in open steam showed the predominating influence of the reclaiming medium and its acidity and alkalinity on the course of these reactions. No change could be observed in the unsaturation of water-digested or metallic chloride-digested reclaims, and only a very small amount of unsaturation appeared lost at and beyond nine hours of heating at 196° C in alkaline medium or in open steam. It was felt, however, that the value obtained for the unsaturation of the various reclaims, even though composed of two or more check analyses in each case, might not reflect the permanent introduction of small percentages of oxygen into the rubber molecule. The presence of even small percentages of C=O and COH groups would, however, be detectable by infrared analysis.

INFRARED SPECTROGRAPHY

For examination by infrared spectroscopy, four reclaims were prepared by heating the pure-gum compound previously studied[1] in finely comminuted condition, in the absence of any reclaiming oils, for nine hours at 196° C in a digester[1] in the presence of either alkali, water, or metallic chloride solutions and also in open steam (heater). These reclaims were washed to pH of 7, dried in vacuum, sheeted out on a rubber mill, and fastened on a framelike sample holder of 1 × 2-inch size. Experiments showed that a sheet thickness of 0.003–0.005 inch was adequate in its infrared transparency. Other investigators[2] had also reported this range of thickness as appropriate in transparency when studying pure-gum compounds.

This method was preferred to the formation of a film by evaporation of a rubber solution because, in the case of reclaim and particularly of reclaims prepared in the presence of metallic chlorides, such film formation would have involved the use of mechanical force to achieve adequate dispersion of the reclaim in the solvent. Care was taken to permit a time interval of 4–6 weeks between the sheeting out of the samples and their infrared analysis. Hydroperoxides which were undoubtedly formed during the mill sheeting[3] would have deteriorated within that period and thus would not appear in the infrared absorption spectrum. The smoked sheet from which the natural-rubber gum

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compound had been originally prepared, as well as the various compounding ingredients, and the unvulcanized and vulcanized compound were also subjected to infrared analysis. Acetone extraction of the samples, however, was avoided because of the great susceptibility of the alkali-treated rubber to oxidation after complete extraction.

While the unvulcanized and also the vulcanized natural-rubber gum compound showed, as usual[4], some absorption at 2.7μ (OH group) and at 5.8μ (C=O group), hardly any trace could be found in the spectra of the water-digester and metallic chloride-digester reclaims prepared from it. The heater reclaim, however, and, more so, the alkali-digester reclaim showed some absorption in these regions, though not so much as either the unvulcanized or the vulcanized original compound. (The storage stability of alkali reclaims—as discussed and shown later on—is smaller than that of metallic chloride or water-digester reclaims). The presence of aldehyde groups in the reclaims could not be determined because of the closeness of the aldehyde absorption band to that of the C=O absorption band. The absorption band at 6.5μ previously found in gum compounds[5] and attributed to impurities[6] was also found in the spectra of the present samples. Fat acids show strong absorption at 6.5μ. The pure-gum compound used for this investigation contained stearic acid, and the samples had not been acetone-extracted for reasons mentioned above.

It is interesting to note that, in the spectrum of the alkali reclaim, this band appeared to shift to 6.36μ. This would seem to make the explanation advanced for it by other investigators[6] plausible, particularly if it is kept in mind that these samples had not been extracted with acetone.

The possibility of either intermolecular or intramolecular ether linkages (C—O—C) cannot be determined at present because the various vibrational possibilities of such a group have not yet been clearly established. If such linkage should occur, however, it cannot be to any greater extent at the double bond, because no loss in unsaturation was found for metallic chloride or water-digested reclaims, and only a small loss in unsaturation in alkali or open steam reclaims. Should such ether linkage occur to any greater extent at the α carbon atom, we could expect that revulcanization of the reclaim and quantitative oxidation of the reclaim by chromic acid[7] should be affected by it. Even though the accuracy of this latter oxidation method cannot be compared with that of infrared analysis, the data available[8] at this time show that, unless reclaiming is carried out under exaggerated oxygenating conditions, the quantitative oxidation of reclaimed rubber by chromic acid is very close to that of vulcanized rubber. The possibility, however, of an ether linkage cannot yet be ruled out completely.

From the chemical data previously obtained[1], as well as from the spectroscopic data, it can be concluded that permanent oxidation of the rubber molecules plays a very small part in the reclaiming reactions, if indeed it occurs at all. Keeping in mind, however, the important role which oxygen has been found to play in the reclaiming processes[9], it can be concluded also that oxygen does exert a temporary influence, by taking part in reactions which do not lead to its permanent introduction into the rubber molecules, provided, of course, that the reclaiming process is not conducted under exaggerated oxygenating conditions. (A reclaiming time interval of nine hours at 196° C in the digester can be considered as one in fairly general use throughout the reclaiming industry. Heater reclaiming during such an interval and at such a temperature is, however, longer than usually practiced.)

THE EFFECT OF SOLVENT NAPHTHA

Experiments carried out about two decades ago[10] have shown that the tensile strength of a vulcanized tread compound deteriorates very rapidly as the temperature and the time of heating in open steam are increased. These experiments were repeated to see whether progress in the art of compounding with respect to vulcanization might have caused any essential change in breakdown of the physical properties of the rubber compound. Results very similar to the original experiments were obtained. However, when the tread compound was first immersed in solvent naphtha until approximately 15 per cent of it by weight had been taken up and was then subjected to the same heat treatment, there was less deterioration in physical properties up to heating periods of nine hours at 196° C. Therefore it seemed of interest to determine the effect of solvent naphtha on the molecular breakdown of the rubber hydrocarbon during reclaiming. It is well known that the proportion of solvent naphtha used for reclaiming depends on the time and the temperature of reclaiming as well as on the state of cure of the scrap and the compounding ingredients contained in it.

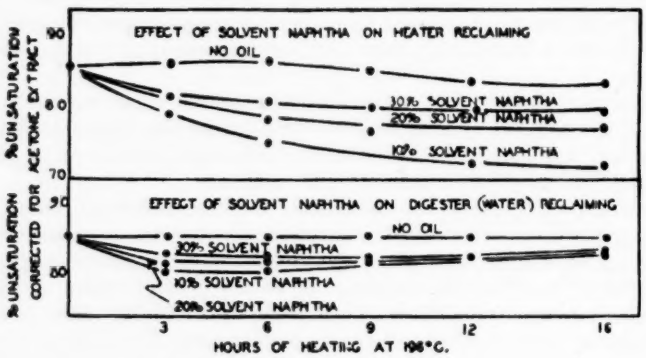

FIG. 1.

For the purpose of evaluating the effect of solvent naphtha on the reclaiming reaction, from 10–30 per cent was added to a natural-rubber gum compound whose reclaiming reactions without the addition of oils had previously been studied[1]. The solvent used was coal tar naphtha. This range was considered large enough to cover the range of 5–15 per cent of solvent naphtha usually added to filler-loaded scrap during practical reclaiming operations. The solvent naphtha was slowly added to the scrap while being stirred and before the addition of any defibering agents. Reclaiming was carried out in the digester in the presence of water, metallic chloride, or alkali, and also in open steam (heater). Washing, drying, and analyses of the reclaims obtained in this way were carried out as already described[1]. It is to be understood, however, that the percentages of solvent naphtha recorded are only approximate, since some evaporation is bound to take place even during the short time between mixing and actual reclaiming.

Figure 1 shows the effect of solvent naphtha on the unsaturation of the reclaims prepared in open steam and in a digester (water). A decrease in unsaturation of the rubber will be noted in both cases; however, the reclaim prepared in the digester (water) shows less decrease in unsaturation than that prepared in the heater. Reclaims prepared in the presence of 10 per cent

solvent naphtha exhibit less unsaturation than those prepared in the presence of 20 per cent solvent naphtha, and the latter gives less unsaturation than reclaims prepared in the presence of 30 per cent solvent naphtha. Thus unsaturation of the reclaim increases again as the percentage of solvent naphtha is increased, but it does not reach the value originally obtained for reclaims prepared without solvent naphtha. The acetone extracts of these reclaims hardly change at all after an initial increase. The curves for the chloroform extracts (Figure 2) show that progressively increasing proportions of solvent naphtha cause a progressive increase in the chloroform extract of the digester reclaims.

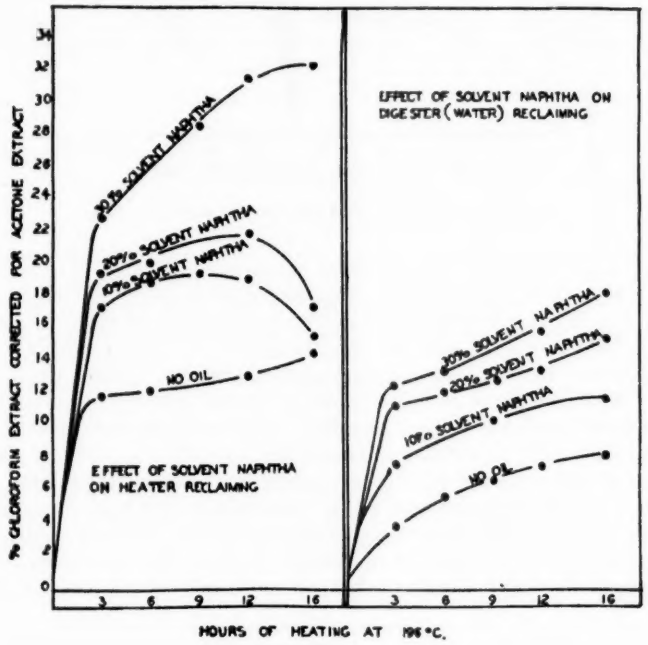
% CHLOROFORM EXTRACT CORRECTED FOR ACETONE EXTRACT
30% SOLVENT NAPHTHA
20% SOLVENT NAPHTHA
10% SOLVENT NAPHTHA
NO OIL
EFFECT OF SOLVENT NAPHTHA ON HEATER RECLAIMING
EFFECT OF SOLVENT NAPHTHA ON DIGESTER (WATER) RECLAIMING
30% SOLVENT NAPHTHA
20% SOLVENT NAPHTHA
10% SOLVENT NAPHTHA
NO OIL
HOURS OF HEATING AT 196 °C.

FIG. 2.

The rate of chloroform extraction was found to be highest for short reclaiming intervals. The rate of molecular breakdown, however, increases even for longer periods of reclaiming as the proportion of solvent naphtha is increased. While this increase in total chloroform extractable substances due to solvent naphtha is considerable for digester-water reclaims, it cannot compete with the great increase in molecular breakdown obtained under identical conditions but for reclaims prepared in the heater.

It was of interest to study the changes which solvent naphtha might bring about in the reclaiming reactions in acid or alkaline defibering media (Figure 3.) Although in each case solvent naphtha increased considerably the molecular breakdown, the overall trend and grouping of the curves, as previously observed for reclaims prepared in the absence of solvent naphtha, did not change. If the curves obtained for the unsaturation values of the water-digester and alkali-digester reclaims obtained in the presence and absence of solvent naphtha

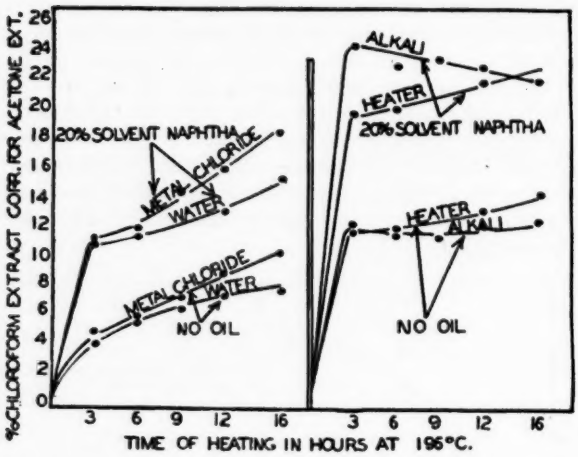

FIG. 3.—Influence of solvent naphtha and defibering agents.

(Figure 4) are compared, the identical trend becomes still more evident. It can again be concluded, therefore, that the course of the reclaiming reaction is conditioned by the acidity or alkalinity, of the surrounding medium, and is accelerated and amplified only by the presence of solvent naphtha.

The decrease in unsaturation and particularly the greater decrease in unsaturation obtained from reclaims prepared in the presence of smaller proportions of solvent naphtha appear puzzling and can be explained on a tentative basis only. Keeping in mind that part which oxygen undoubtedly plays in the reclaiming of natural rubber, we can expect that access to oxygen would be greater in a rubber polymer where the molecular chains have been pried apart to a certain extent. The absorption of 10 per cent of solvent naphtha does not, however, permit a great amount of prying apart of the molecules, nor is all of the space between the molecules taken up uniformly by solvent naphtha mole-

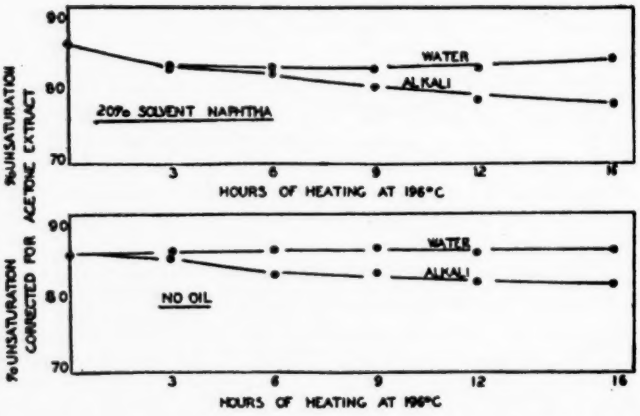

FIG. 4.—Unsaturation values for water- and alkali-digester reclaims with and without solvent naphtha.

cules. This nonuniformity causes some strain and deformation of some of the rubber molecules. If oxygen accessibility plays any part in the reclaiming reaction, we would expect a greater decrease in unsaturation in the reclaim prepared in open steam (heater) in the presence of smaller proportions of solvent naphtha than in a digester-water reclaim of similarly composition. The experimental results seem to bear this point out. It is impossible for the moment to determine what kind of change has taken place in the rubber molecule to cause the decrease in unsaturation. Intramolecular bridging appears less plausible than intermolecular bridging. Infrared analysis might give a clue to the kind of reaction which occurred; however, the possibility cannot be dismissed that, despite careful acetone extraction, some component of the solvent naphtha may remain in the reclaim, even if only in very small proportions, and thus disturb the interpretation of an infrared spectrogram. It seems fairly improbable, though, to expect this decrease in unsaturation to be caused by a primary chemical bond between rubber and solvent naphtha molecules. If this were to occur, we could certainly expect the reclaims prepared in the presence of 20 and 30 per cent solvent naphtha to show a decrease in unsaturation still more pronounced than that obtained with 10 per cent solvent naphtha. Actually the opposite condition exists, as shown by the experimental data. As the percentage of solvent naphtha is increased, the rubber chains are pried farther and farther apart, and distribution of the solvent naphtha molecules between the rubber chains can be considered to become more uniform. Therefore reactions between the rubber molecules are less likely to occur, because combination by chemical forces becomes more difficult as the distances between two rubber molecules increase. Furthermore, the greater proportions of solvent naphtha molecules can be expected to have a blocking effect.

EFFECT OF RECLAIM STORAGE

The practical effects of storage on reclaim are well known. In general, a decrease in chloroform extract has been noticed. The phenomenon was studied in greater detail over a period of weeks with two whole-tire reclaims[11]. Tire reclaims, however, contain carbon black, and the insolubilization of the low molecular rubber hydrocarbon component by carbon black is a phenomenon encountered both in synthetic as well as in natural rubber carbon black compounding. Therefore the decrease in the chloroform extract of whole-tire reclaims may be due at least to three factors: reclaiming oils, carbon black, and instability of the reclaim rubber hydrocarbon itself. The latter factor can cause either a decrease or increase in chloroform extract of the reclaim. If the reclaiming reactions proceed on the basis of hydroperoxidic chain reactions, instability of the rubber hydrocarbon during storage can be expected. Also, such instability should tend to increase the amount of chloroform extract during storage. On the basis of this condition, it would be expected that the shorter the reclaiming interval, the more unstable a reclaim should be produced[1]. Furthermore, it can be expected that, under hydroperoxidic reaction conditions, alkali reclaim should prove the least stable[12] and digester-water and digester-metallic chloride reclaims should be similar in their behavior, but more stable than the former.

An increase in the chloroform extract during storage would not, however, preclude the simultaneous recovery of the reclaim or the chloroform extractable substances in it. Not only might the chloroform extract increase, but the molecular weight of the chloroform extractable rubber might also increase

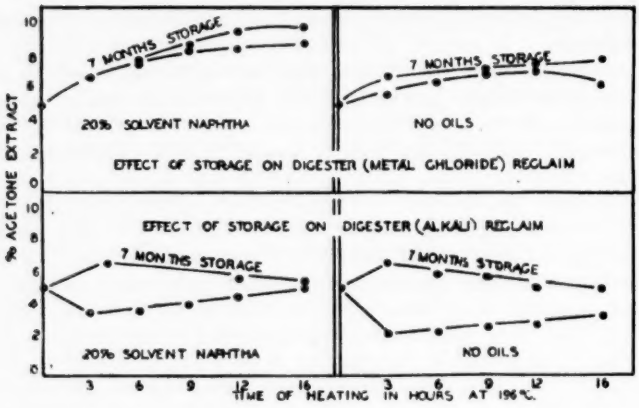
% ACETONE EXTRACT
7 MONTHS STORAGE
20% SOLVENT NAPHTHA
NO OILS
EFFECT OF STORAGE ON DIGESTER (METAL CHLORIDE) RECLAIM
EFFECT OF STORAGE ON DIGESTER (ALKALI) RECLAIM
TIME OF HEATING IN HOURS AT 196°C.

FIG. 5.

during storage. Chloroform is known to be an excellent solvent for rubber hydrocarbon, and for this reason is not used in the fractionation of the latter. It is possible that the chloroform extractable fraction of the reclaim increases in molecular weight, yet remains soluble in chloroform. Viscosity determinations of the chloroform extract would probably answer this question.

To study the effect of storage on the reclaim hydrocarbon, the digester (alkali, water, or metallic chloride) reclaims and the open steam (heater) reclaims prepared for a previous study[1] were stored at 80° F and 50 per cent moisture for seven months. Reclaims prepared in the presence of 20 per cent solvent naphtha and described above were likewise stored. Figure 5 shows the acetone extracts from the metallic chloride and alkali treated reclaims. The metallic chloride-digester reclaim exhibits a slight increase in the acetone extract during storage. The presence or absence of 20 per cent solvent naphtha during reclaiming does not seem to affect this condition to any great extent. The alkali-digester reclaim shows a considerable increase in acetone extractable substances during storage; the greatest increase occurs in reclaims subjected to short reclaiming times. Solvent naphtha appears to exert a stabilizing influence on the formation of acetone extractable substances. The increase in acetone extract, though still pronounced and still greater for short reclaiming

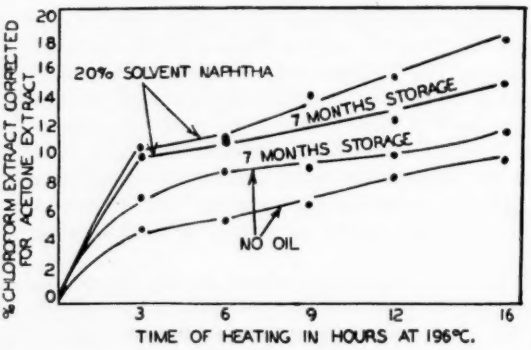
% CHLOROFORM EXTRACT CORRECTED FOR ACETONE EXTRACT
20% SOLVENT NAPHTHA
7 MONTHS STORAGE
7 MONTHS STORAGE
NO OIL
TIME OF HEATING IN HOURS AT 196°C.

FIG. 6.—Effect of storage on digester (metal chloride) reclaim.

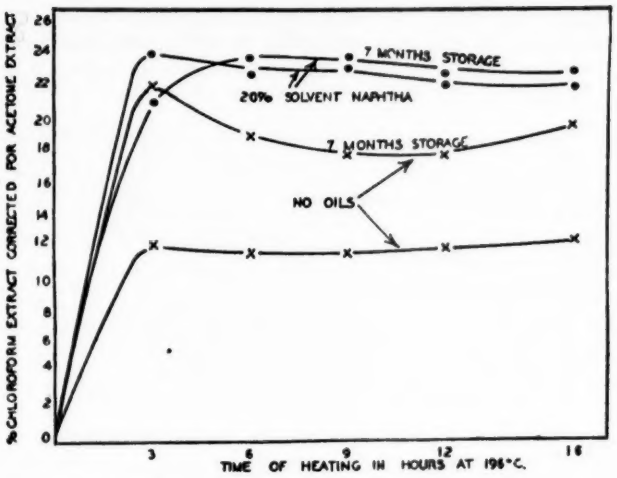
% CHLOROFORM EXTRACT CORRECTED FOR ACETONE EXTRACT
7 MONTHS STORAGE
20% SOLVENT NAPHTHA
7 MONTHS STORAGE
NO OILS
TIME OF HEATING IN HOURS AT 196°C.

FIG. 7.—Effect of storage on digester (alkali) reclaim.

times, is not so great as that of the reclaims prepared in the absence of solvent naphtha.

Figure 6 shows the change in chloroform extract in metallic chloride-digester reclaim during an identical storage period. The chloroform extract has increased, and again the presence of solvent naphtha during reclaiming appears to stabilize the reclaim. Figure 7 records the results obtained from the storage of alkali-digester reclaim. The increase in the chloroform extract of the reclaims prepared without solvent naphtha is considerable; the greatest increase occurs in those alkali reclaims subjected to short reclaiming periods. The presence of solvent naphtha during reclaiming, however, exerts a pronounced stabilizing effect on the molecular breakdown during storage. The chloroform extracts of the fresh and the stored reclaim remain almost constant. Figure 8 represents the data obtained for the acetone extracts of water-digester reclaim. While the water-digester reclaim prepared in the absence of oils exhibits a noticeable increase in the acetone extract during storage, this effect seems blocked, and the reclaim appears stabilized by reclamation in the presence of solvent naphtha. Figure 9 represents data obtained for the chloroform extract of the two corresponding water-digester reclaims. Here too the increase in chloroform extract during storage of the reclaim prepared in the

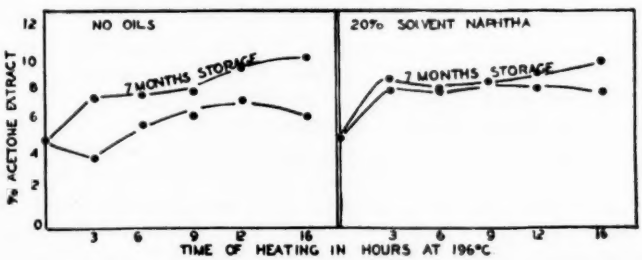

FIG. 8.—Effect of storage on digester (water) reclaim.

absence of solvent naphtha is appreciable. The greatest increase in chloroform extract again occurs in reclaims subjected to short reclaiming periods. The same kind of reclaim prepared in the presence of solvent naphtha is much more stable.

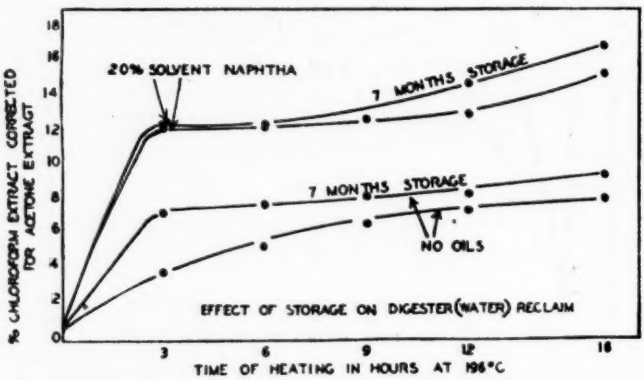

FIG. 9.

Reclaims prepared in open steam (heater) with or without solvent naphtha show little change in their chloroform extracts during storage. Formation of a considerable amount of acetone extractable substances, however, can be noticed during storage, regardless of whether the reclaim was prepared in the presence or absence of solvent naphtha.

A decrease in unsaturation of all the reclaims occurs during storage. This decrease is small, yet is consistent and equal for reclaims prepared in the presence of solvent naphtha. Table 1 records the values obtained for reclaims three weeks and seven months of age.

TABLE 1

PERCENTAGE UNSATURATION CORRECTED FOR ACETONE EXTRACT

Hours of heating at 196° C	Digester alkali		Digester water		Digester metallic chloride		Open steam heater	
	3 Wks.	7 Mos.	3 Wks.	7 Mos.	3 Wks.	7 Mos.	3 Wks.	7 Mos.
3	86.3	83.5	86.5	80.0	86.5	—	86.5	—
6	84.5	82.5	86.5	81.5	—	80.5	86.5	85.0
9	84.0	82.0	86.8	82.0	87.0	81.0	86.0	84.5
12	83.3	77.0	86.0	82.5	86.5	—	84.5	78.5
16	83.0	76.5	87.0	83.0	86.0	83.5	83.0	76.0

Storage of the chloroform-extractable rubber hydrocarbon over a period of seven months hardly changed its unsaturation.

From the data on the stability of reclaim during storage, it can be concluded that solvent naphtha exerts a stabilizing influence on digester (alkali, water, or metallic chloride) reclaims. The decrease usually noticed in the chloroform extract of production reclaims may be due to rearrangement of the carbon black dispersion during storage and also to the influence of the reclaiming oils. The changes which take place during the storage of reclaim are influenced by the acidity and the alkalinity of the medium in which the reclaiming was

originally conducted. Short reclaiming times, as expected, result in reclaims of greater instability on storage.

EFFECT OF AGING OF THE SCRAP BEFORE RECLAMATION

It has long been known to the reclaimer that scrap which has been more oxidized during use can be reclaimed with greater ease. None of the present aging tests, however, fully simulate the aging of rubber under service conditions. To study the effect of aging of scrap on reclaiming, a medium of artificial aging was desired which would not permit too uneven an attack on the rubber by oxygen. It was decided, therefore, to use a Geer oven at 70° C for 160 hours. The natural-rubber compound previously described[1] increased from 5.4 to 6.3 per cent in acetone extract during this aging period. The chloroform extract increased from 0.6 to 2 per cent, but the unsaturation remained steady. The scrap was permitted to recover for at least 24 hours after aging before it was subjected to grinding and reclaiming.

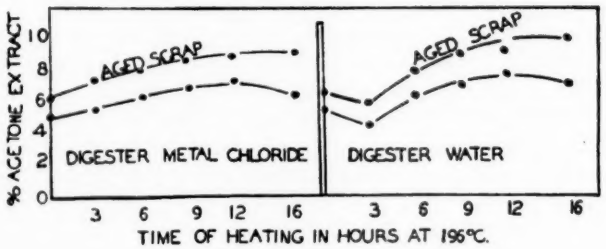

FIG. 10.—Effect of aging of scrap.

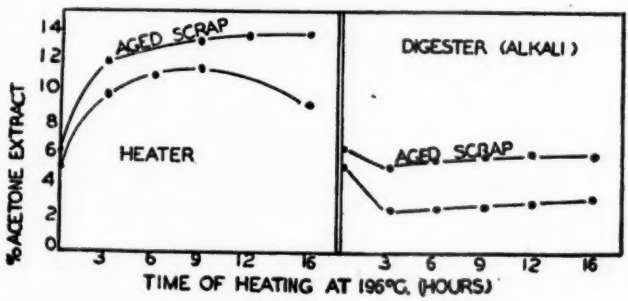

FIG. 11.—Effect of aging of scrap.

Figures 10 and 11 record the effect of aging scrap on the formation of acetone extract during various reclaiming processes. The two curves for the fresh and the aged scrap run almost parallel in the case of the water-digester and metallic chloride-digester reclaims; the formation of acetone extractable substances during reclaiming is only slightly influenced by the oxidation which takes place before reclaiming. If, however, aged scrap is reclaimed in the digester in the presence of alkali, a considerable amount of acetone extractable substances is formed during reclaiming. Figure 12 shows the effect of aging scrap before reclaiming on the chloroform extract of the reclaim. The chloroform extract of the digester (water or metallic chloride) reclaims is increased by aging the scrap.

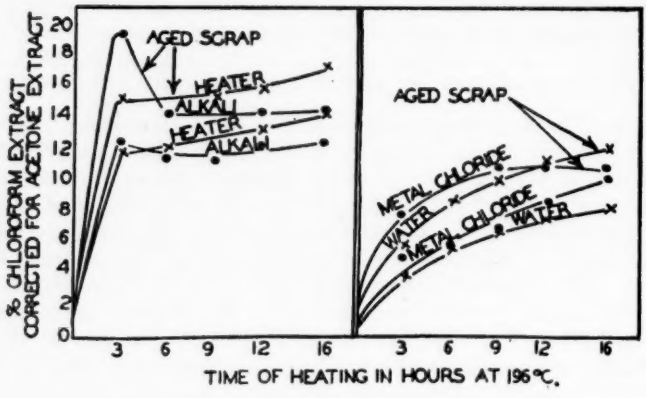

FIG. 12.—Effect of aging of scrap.

The greatest increase in chloroform extract, however, is found for alkali digester reclaim and, in particular, for the short reclaiming times of this reclaim. This indicates that a small amount of secondary oxidative attack of the rubber hydrocarbon facilitates molecular breakdown. The possibility of such a reaction has already been mentioned[12]. Aging of scrap before reclamation, however, does not affect the relative position of the curves; *i.e.*, the surrounding atmosphere during the reclaiming process still has a dominant influence on the reclaiming reactions.

The unsaturation of reclaims prepared from aged scrap is hardly different from that of reclaims prepared from fresh scrap. It can be expected, however, that if aging is carried to a greater extent, changes in the unsaturation of the reclaims would occur.

SUMMARY AND CONCLUSIONS

Infrared analyses of digester (alkali, water, or metallic chloride) reclaims and of heater reclaim show that permanent combination of oxygen with rubber hydrocarbon molecules with formation of C=O or OH groups does not occur during the reclaiming of natural rubber. It is not possible to detect the formation of C—O—C bonds. Chemical considerations indicate that, if such bonds are formed, they are not present to any great extent.

The presence of solvent naphtha during reclaiming decreases the unsaturation of both digester and heater reclaims. This decrease is greater if small amounts of solvent naphtha are present. A tentative explanation, based on the swelling of the rubber and taking into account the strong dependency of the chemical bond formation on the distances between the molecules, is offered.

Molecular breakdown of the rubber is highly accelerated and amplified by the presence of solvent naphtha, but the course of the reclaiming reactions are not changed, and they still depend on the surrounding reclaiming medium and its acidity or alkalinity.

The stability of reclaims during storage is also influenced by the surrounding medium during the original reclaiming. Short reclaiming times and alkaline reclaiming media give the least stable reclaims. Such behavior can be expected if hydroperoxidic chain reactions take place during the reclaiming processes.

The presence of solvent naphtha during the reclaiming process brings about greater stability of the reclaim during storage.

Aging of scrap before reclaiming promotes greater molecular breakdown, particularly during short reclaiming times and in the presence of alkali.

ACKNOWLEDGMENT

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REFERENCES

[1] *India Rubber World* **118**, 59 (1948); RUBBER CHEM. TECH. **21**, 895 (1948).
[2] Sheppard and Sutherland, *Trans. Faraday Soc.* **41**, 261 (1945).
[3] Busse, *Ind. Eng. Chem.* **24**, 140 (1931); Cotton, *Trans. Inst. Rubber Ind.* **21**, 153 (1945).
[4] Barnes, Liddell, and Williams, *Ind. Eng. Chem. Anal. Ed.* **15**, 83 (1943); Dinsmore and Smith, *Anal. Chem.* **20**, 11 (1948).
[5] Sheppard and Sutherland, *Trans. Faraday Soc.* **41**, 261 (1945); Dinsmore and Smith, *Anal. Chem.* **20**, 11 (1948).
[6] Dinsmore and Smith, *Anal. Ed.* **20**, 11 (1948).
[7] Burger, RUBBER CHEM. TECH. **16**, 660 (1943).
[8] Le Beau, *Anal. Chem.* **20**, 355 (1948).
[9] Palmer and Kilbourne, *Ind. Eng. Chem.* **32**, 512 (1940); Kirbe and Steinle, U. S. patent 2,279,047 (1942).
[10] Winkelmann, *Ind. Eng. Chem.* **18**, 1163 (1926).
[11] Palmer and Kilbourne, *Ind. Eng. Chem.* **32**, 512 (1940).
[12] Farmer, *India Rubber J.* **112**, 119 (1947).

ANALYSIS OF NATURAL AND SYNTHETIC RUBBER BY INFRARED SPECTROSCOPY *

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NAVAL RESEARCH LABORATORY, WASHINGTON, D. C.

This report describes an investigation of the applicability of infrared spectroscopic methods to the quantitative determination of the elastomer composition of industrial rubber products. Generally satisfactory techniques for obtaining a valid spectrum of the elastomer content of any rubber specimen have been developed and evaluated and have been applied to the development of detailed analytical procedures for the identification and qualitative analysis of elastomer mixtures, to the quantitative analysis of natural-GR-S blends, and to the determination of the nitrile content of nitrile copolymers. An accuracy corresponding to ±1 per cent average error has been obtained in these determinations. The methods can be extended to analogous problems with a minimum of alteration, and the same order of accuracy can be expected in general. A discussion of the correlations between spectral absorption and molecular structure is also included.

Infrared spectroscopy is finding increasing application as a means for the identification of organic materials and the analysis of complex mixtures[1]. Spectroscopic methods are not only rapid and generally conservative in sample requirements, but the results are often more specific than those obtained by chemical analysis, distillation, etc., and in many cases furnish detailed structural information of importance to research and development. The advantages of infrared analysis are that: (1) the spectrum of a molecule is a unique physical property which is not altered by any changes in which molecular identity is maintained, and (2) the individual features of the spectrum relate in a definite manner to the chemical bonds comprising the molecule and can thus be interpreted, regardless of the total configuration.

Procedures for the accurate determination of the identities and proportions of the elastomers present in a finished product are needed throughout the rubber industry for control and specification. With the ever-growing number and variety of substitutes for rubber and special-purpose synthetics incorporated in manufactured goods, either singly or as blends, the problem facing the rubber analyst has become increasingly complex and well beyond the scope of conventional chemical methods. In addition, analytical methods which allow the study of polymer structure should prove significant in the development of new polymers and in the evaluation of polymerization techniques.

Several investigators have recognized the advantages of employing a physical means of investigation by which the various types of chemically inert molecular structures in polymers can be studied without changing their identities or proportions. Infrared methods have been significant, for example,

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in exploring the mechanism of polymer formation[2] and in studying vulcanization[3] and oxidation[4]. Considerably less has been done to develop infrared methods into routine procedures for specifications of rubber products. This is undoubtedly due, in a large part, to experimental difficulties encountered in the spectroscopic examination of vulcanized and reënforced rubbers. An attempt to overcome these difficulties was made by Barnes and coworkers[5], who developed a procedure for the analysis of natural rubber-Buna-S blends in tread, carcass, and tube stocks. Although their results were satisfactory for purposes of the study, the accuracy did not appear as good as might be expected, and the data presented did not permit any conclusive evaluation of the procedure, particularly in regard to the extension of the method to other elastomers.

This paper describes the results of an extensive study of the applicability and limitations of infrared methods for the identification and quantitative analysis of the elastomer content of commercial articles of natural rubber and some of the common synthetics. The first phase of the work was concerned with determining valid absorption spectra of the various pure elastomers. These reference spectra were required to evaluate the spectral basis for identification of elastomers and for later use in identifying any spectral effects not directly related to elastomer composition. A second phase was concerned both with the development of a satisfactory technique for spectral examination of a compounded and cured rubber and with the determination of the extent to which the spectral absorption so obtained is related to elastomer composition, as distinguished from other spectral effects of the history or state of the sample, etc. The necessity of removing fillers which render the sample too opaque for quantitative spectral study and the additional advantages of eliminating all effects of nonrubber components from the spectral results dictated the use of procedures involving isolation of the elastomer content as a preliminary step. In this connection, solvents for cured elastomers and methods for removal of colloidal carbon from rubber solutions have received special attention. A third phase was concerned with the development and evaluation of detailed procedures for certain analyses which are of practical importance and which illustrate the general feasibility of quantitative applications.

GUM ELASTOMERS

The problem of determining reference spectra, *i.e.*, the correct spectrum of the pure rubber hydrocarbon, is best approached by the study of gum rubbers wherein the elastomer chains are already large compared with the polymerizing units (or monomers), but where modifying effects such as may accompany compounding, curing, aging, etc., have not yet been introduced. Thirteen gum samples comprising seven different classes of elastomers were used for this purpose. The samples were 97 per cent pure elastomer, the remainder chiefly antioxidant, and were as follows: Natural smoked sheet rubber, Lee pure-gum cement, tube reclaim, GR-I, Neoprene-GN, Neoprene-ILS, GR-S, Chemigum N-1, Hycar-OR-15, Butaprene-NF, Perbunan-35, Thiokol FA, and Thiokol-RD.

Preparation of the sample.—The gum samples were prepared for spectroscopic examination by: (1) solvent extraction of antioxidant and all soluble impurities; (2) solution of the elastomer in a suitable solvent; (3) removal of excess solvent by evaporation; and (4) preparation of films on rock salt or potassium bromide plates for spectroscopic study. Commercial grade ethyl alcohol (95 per cent) was used for extraction in the standard A.S.T.M. rubber

extraction assembly (1) consisting of 400-cc. flask, siphon cup, and water-cooled tin-coil condenser. Solubility and ensuing gelation prohibited the use of other solvents such as benzene, chloroform, and acetone. A 2-gram sample was cut into thin strips and placed in parallel rows on a filter paper, so as not to be in contact when the paper was rolled. Two or three 80-cc. portions of solvent were used, and the progress of extraction was followed by noting the coloration. On the basis of subsequent spectra, continuous extraction for 24 hours was shown to be sufficient.

Solutions of the various elastomers were made at room temperature to minimize possible decomposition or alteration of the elastomer. The solvents used were of standard technical grade, and contained no nonvolatile substances. Of the solvents investigated, only ethylene dichloride satisfactorily dissolved all the elastomers studied, including the Neoprenes. Methylethyl ketone was very effective for nitrile copolymers, but not for the others. Natural rubber, Thiokol-FA, GR-I (Butyl), and GR-S dissolved readily in several solvents. The average requirement was 40 to 60 cc. of solvent per gram of rubber. The solutions obtained were transparent, but exhibited light colors, probably from oxidation. Solution of the more soluble elastomers was accomplished merely by 6 to 8 hours' mechanical shaking of the rubber with solvent. This simple technique did not prove satisfactory for Neoprene and nitrile copolymer types because of the persistence of a gelatinous structure despite the use of excessive quantities of solvent. Solution was accomplished far more rapidly and effectively by mixing rubber and solvent in a Waring Blendor[6]. (All rubber gaskets were replaced by gaskets of felt between outer ones of lead.) This technique readily reduced gels to thin homogeneous mixtures and permitted satisfactory preparation of all samples in a minimum quantity of solvent. Generally, the rubber was allowed to soften and swell in the solvent for 2 hours, then blendorized for 10 to 20 minutes. Tube reclaim was treated as an exception to the gum samples, since it contained a mineral filler and was considerably less soluble. It was extracted by a 32–68 blend of acetone-chloroform, and was dissolved by refluxing with a 20–80 blend of xylene and *p*-cymene. The filler was removed by centrifugation.

The solution of polymer was concentrated to a viscous mucilage suitable for film spreading by evaporation on an A.S.T.M. gum bath at 80° C. Stirring by hand adequately eliminated gel formation resulting from localized surface evaporation. Although vacuum distillation was also employed successfully, the former method was preferred, for it permitted simultaneous evaporation of several solutions. Films of uniform thickness were prepared on sodium chloride or potassium bromide plates by spreading the concentrated mucilage between parallel spacers, as shown in Figure 1. Thirty minutes' standing was allowed for final solvent evaporation. The appropriate film thickness for useful spectroscopic measurements was determined by trial preparation of films of several thicknesses and subsequent spectral measurement at the common 6.9 mu carbon-hydrogen band, where the absorption should be between 80 and 90 per cent. Three sets of spacers—0.05, 0.10, and 0.20 mm.—enabled suitable films to be obtained in all cases. In the case of nitrile copolymer samples, solvent removal was generally stopped prematurely to avoid serious gelation, and films of suitable thickness were obtained by spreading successive films on one another.

All spectroscopic measurements were made using a large recording prism spectrometer of high resolving power[7]. As recorded, the spectra consisted of a pair of traces measuring (as percentage full-scale) the energy transmitted by

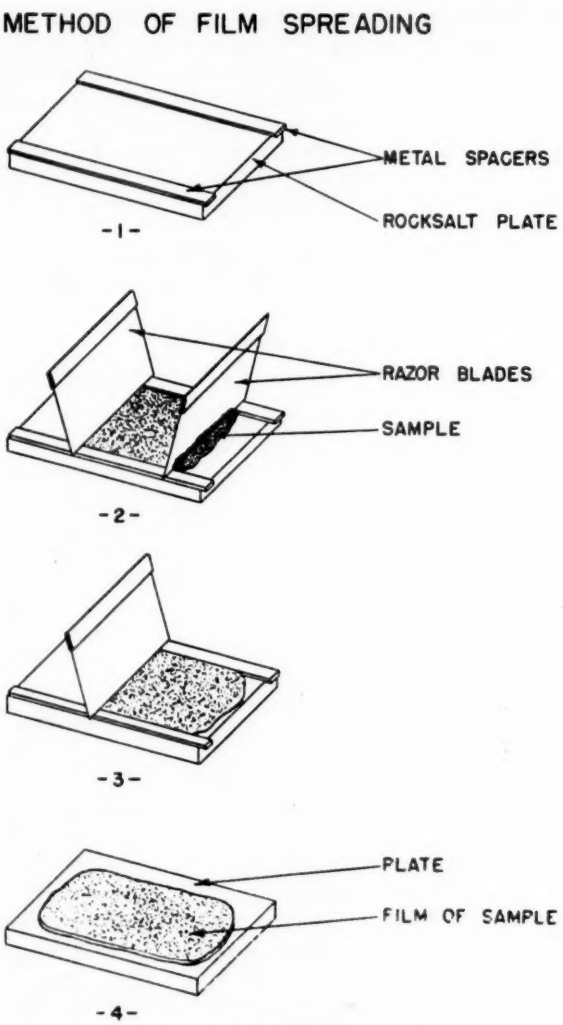


FIG. 1.—Method of film spreading.

the sample and by a blank plate as a function of wave length (on a nonlinear scale). A percentage transmittance spectrum of the sample was obtained by measuring the ratios of corresponding ordinates, and the spectrum was transcribed (using calibration data) to linear wave-length charts. Under normal operating conditions, wave-length measurements were considered accurate to ±0.01 mu from 2 to 15 mu, and percentage transmittance measurements were reproducible to about ±1.0 per cent.

Discussion of results.—Several satisfactory spectra were obtained over the 2- to 14-micron range for each elastomer studied. Beyond 14 mu the absorption was too weak for analytical purposes, and the results are not included. A set of these reference spectra shown in Figure 2 establishes the fact that the

seven different classes of rubber examined possess characteristically different spectra. The qualitative spectral differences correspond to basic differences in polymer structures, and furnish an adequate basis for spectroscopic identification of each class. On the other hand, close similarity exists among the spectra of elastomers which are members of the same basic class of polymer or copolymer, as for the two Neoprene polymers or the five nitrile copolymers (not all shown). The differences here are quantitative and, though less obvious, are significant if the proportions of the various structures comprising the elastomer are of interest.

In addition to the fact that the use of pure samples assured good reference spectra, the validity of the spectra obtained was established by their close

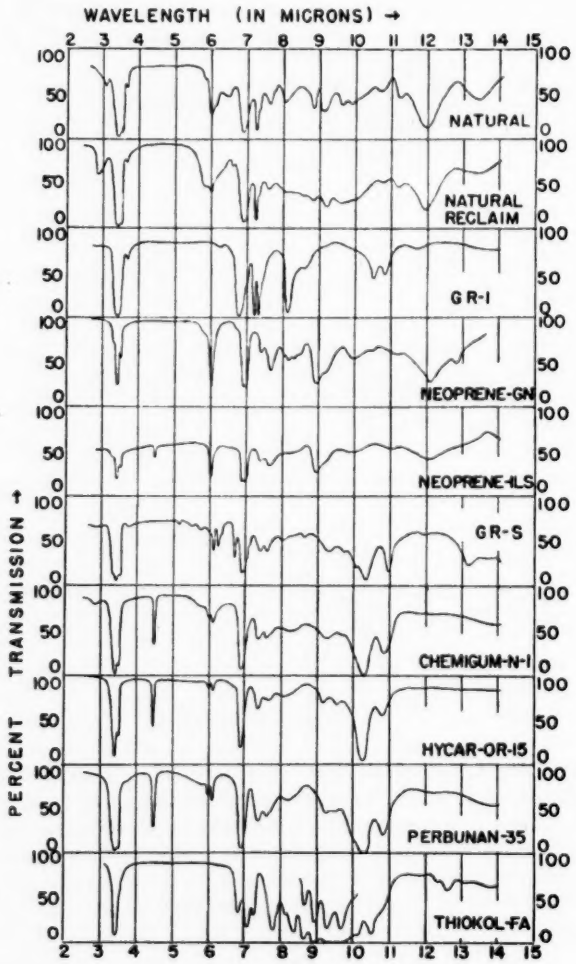


FIG. 2 - SPECTRA OF PURE GUM ELASTOMERS

Fig. 2.—Spectra of pure gum elastomers.

reproducibility during extensive duplication of sample preparation and spectral measurement. For nearly all preparations, duplicate films were studied to determine the reproducibility in film preparation and spectroscopic measurement. In several cases the entire preparation was carried out in duplicate so that the reproducibility of the overall method of study might be established. Finally, a number of samples were prepared by alternative procedures, using different solvents and solution methods, so that the influence, if any, of particular preparation features on the final spectrum might be shown. In all cases (in which the method of preparation was adequate) virtually perfect reproducibility of spectra was obtained, showing definitely the reliability of the overall method of study and the sole dependence of the spectrum on the elastomer itself. The spectra obtained are, therefore, considered accurate reference spectra of the pure rubber hydrocarbons.

COMPOUNDED AND CURED ELASTOMERS

The problem of developing suitable procedures for preparing a commercial rubber product for spectral examination and of determining the spectral accuracy and reproducibility obtainable for differently cured and compounded elastomers was solved by extensive experimental work, involving both duplicate runs and many variations in procedure. A particular aim was to find a single procedure of such scope that in examination of any unknown specimen by this procedure the possibility that any elastomer would escape quantitative treatment would be negligible. In investigating this two-fold problem, eighteen compounded specimens were studied. These specimens were compounded from the gum elastomers previously studied, and included a great variety of mixes and types of cure, which were considered fully representative of industrial products in variety and character. The carbon blacks employed were Thermax, Furnex, Statex-B, and P-33; thirty different accelerators, antioxidants, inhibitors, tackifiers, plasticizers, etc., were used. The maximum sulfur content was 3 per cent, maximum carbon black 50 per cent, maximum zinc oxide 10 per cent, and maximum cure 50 minutes at 300° F. The method used for preparation and study of these specimens comprised: (1) preliminary milling of the sample; (2) extraction of organic additives; (3) solution of the elastomer; (4) removal of the filler; and (5) evaporation of the solvent to obtain a transparent film of pure polymer for spectroscopic examination.

Experimental.—Extraction and solution of the sample were facilitated by preliminary milling. This comprised several passes through a standard roll mill at room temperature, after which the shredded rubber was chopped in a Wiley laboratory mill to pass through a No. 20 screen. A 32–68 blend of acetone-chloroform was used with the standard A.S.T.M. extraction assembly[8] for extraction of organic additives and impurities. Continuous extraction for 24 hours with two or three 80-cc. portions of solvent was satisfactory.

Reflux temperatures above 100° C appeared necessary to dissolve all cured rubbers, especially the Neoprene and nitrile rubbers. Solvents boiling above 190° C, however, were not considered because of the difficulty of subsequent solvent removal and the importance of minimizing decomposition of rubber or solvent which might accompany severe heating. Technical grades of the solvents were distilled before use to eliminate higher-boiling components and gum-forming impurities. Of the solvents investigated, only *o*-dichlorobenzene successfully dissolved all samples, including Neoprene-ILS and the nitrile copolymers, and was eminently satisfactory with respect to purity and inert-

ness on prolonged heating. Tetrachloroethane was used extensively for all cured elastomers except Neoprene-ILS and nitrile rubbers, and, despite traces of free hydrochloric acid which persisted on refluxing, was satisfactorily inert toward the rubber hydrocarbon. *p*-Cymene dissolved all samples except nitrile types, but its use with prolonged refluxing led to oxidation and serious gum formation, which contaminated the sample. Pyridine and nitropropane were ineffective for nitrile rubbers, and several high-boiling ketones precipitate gums in the sample during refluxing.

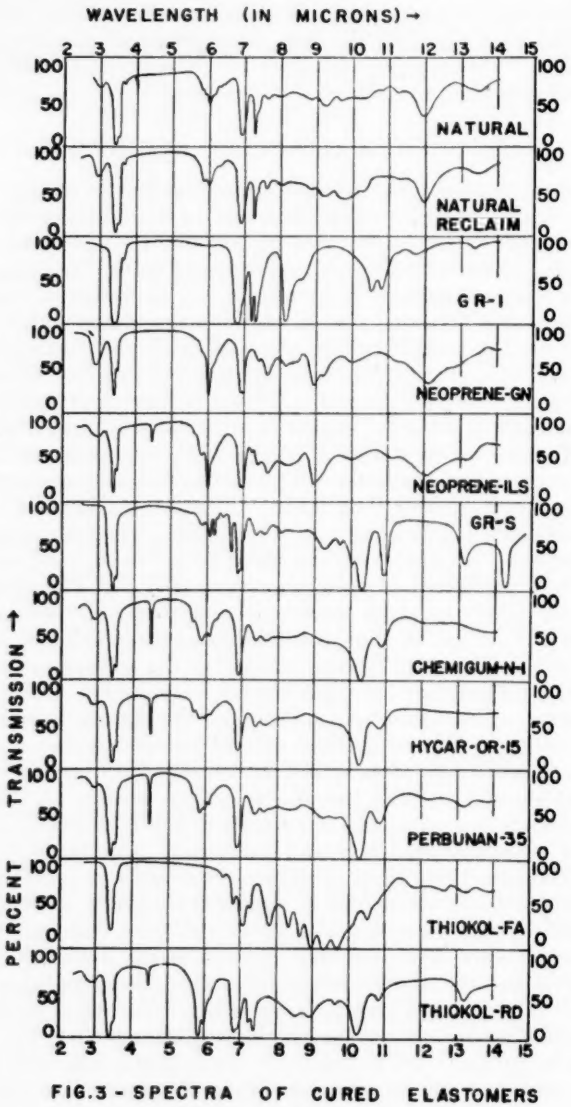


FIG. 3.—Spectra of cured elastomers.

A 4-gram sample and 250 cc. of solvent were refluxed for 24 to 36 hours in an A.S.T.M. condenser and flask assembly or in a similar all-glass assembly, using a water-cooled condenser (Figure 3) designed for this purpose. A glass condenser can be used interchangeably with the A.S.T.M. tin-coil condenser, and is preferred for chemical inertness and ease of cleaning. Complete solution of some of the less soluble elastomers was best accomplished by successive treatment with two or three 100-cc. portions of solvent. Blendorization decreased the time required for solution, but was not essential, since serious gelling never occurred. Absence of appreciable residue after an hour of settling indicated complete solution of the elastomer.

Comparatively coarse fillers, such as clays, iron oxide, etc., were separated by simple centrifugation. This method was ineffective for colloidal carbon blacks. The procedure used by Barnes[5], employing dilution with *n*-hexane, was tested on a series of natural rubber and nitrile rubber samples, but was found to be unreliable because of selective precipitation of the elastomer. Filtration with adsorbents such as bentonite, fuller's earth, alumina, and silica gel was also unsatisfactory. Celite analytical filter aid (Johns-Manville Co.), however, permitted complete removal of colloidal carbon in every case investigated. After the polymer solution had been diluted to 300 cc. with benzene, about 50 to 100 cc. of Celite were added, and the slurry was filtered through a semifine paper. Filtration proceeds most rapidly if sufficient Celite is added so that free carbon does not clog the paper. Trial filtrations with small portions of the slurry readily allow a proper Celite content to be found. Quantitative work with solutions of mixed elastomers showed conclusively no selectivity toward the elastomers. Variations in procedures, such as in the temperature of the solution during filtration, appeared to be of little importance as regards efficiency. Solution holdup in the filter aid is of no importance, but can be recovered nearly completely by adding hot benzene and refiltering.

The elastomer solutions were concentrated by vacuum distillation at 100° to 110° C, using a water aspirator and conventional Claisen-type flask immersed in an oil bath. The viscous concentrate was diluted with a few cc. of benzene and transferred to a small container for storage; the benzene was removed later by evaporation at room temperature or in a vacuum oven at 60° C. Films for spectral examination were spread as before, and 40 minutes in a vacuum oven at 80° C was allowed for final solvent evaporation. Films of natural rubber and Thiokol were sticky but satisfactorily rigid; those of other elastomers were solid and nearly free of tackiness.

Discussion.—Several satisfactory spectra were obtained for each sample studied, and a representative set is shown in Figure 4. Comparison with Figure 2 shows the spectra of a pure-gum elastomer and its vulcanizate to be nearly identical, except for minor differences, which are discussed below. This significant result was obtained consistently throughout more than fifty spectra of separate sample preparations, and in itself is adequate evidence of the validity of all spectra obtained. In addition, almost perfect spectral reproducibility was found for the spectra of each elastomer obtained from duplicate preparations in *o*-dichlorobenzene, and in most cases from additional preparations in *p*-cymene and in tetrachloroethane. The overall method was thus shown to be reliable, and the spectral results obtained were shown to be nearly independent of the sample history, *i.e.*, of compounding and curing effects and of the method of preparation for study.

The complete spectral identity of cured and uncured rubbers is not inconsistent with current concepts of the vulcanization process, which is considered

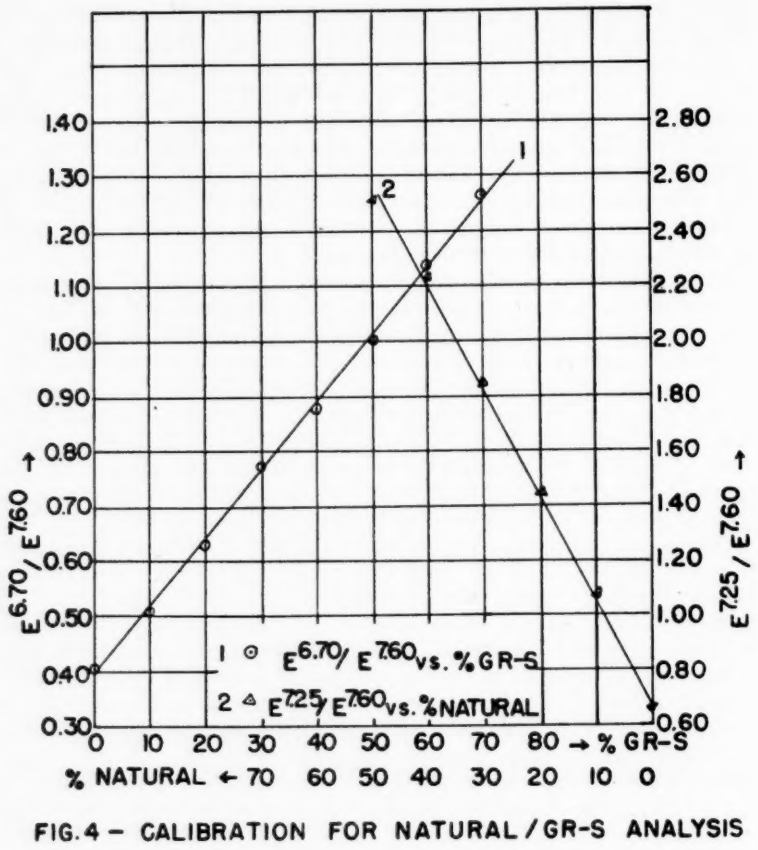


FIG. 4 – CALIBRATION FOR NATURAL / GR-S ANALYSIS

FIG. 4.—Calibration for natural/GR-S analysis.

to introduce comparatively few cross linkages in building the three-dimensional vulcanizate. Since the infrared spectrum of a polymer is determined almost entirely by the small recurring structural units and not by the gross size of the configuration, the net result of vulcanization, consisting mainly of changes which involve relatively few of the recurring polymer units, does not alter the rubber spectrum to any appreciable extent. Only two minor differences between the spectra of raw elastomers and their vulcanizates (Figures 2 and 4) were noticed. In general, oxidation during vulcanization produces hydroxyl absorption near 3.0 mu and carbonyl absorption between 5.6 and 6.0 mu. These extra bands do not interfere, however, with any bands useful for analysis. A more consistent difference is the poorer definition of bands themselves and the increased background absorption beyond 8 mu in the spectra of most cured rubber. This effect has been observed in a homologous series of simple hydrocarbons, and is consistent with the increased molecular weight of the vulcanizate. This absorption was not reproducible for different sample preparations and, though serious only in natural vulcanizates, it cannot be disregarded in quantitative work.

The method of study leaves little to be desired from the spectroscopist's viewpoint, since isolation of the rubber hydrocarbon assures valid results. The method applies to all elastomers investigated and to blends of these elastomers, and a single procedure remarkably free of exacting techniques may be used. Routine application requires about 6 man-hours per sample.

IDENTIFICATION AND QUALITATIVE ANALYSIS

The fact that the spectra of the various elastomers, when obtained by the procedures described, are unique and experimentally reproducible regardless of the past history of the sample constitutes a sound basis for characterization of the elastomer content of commercial rubber products. The individual elastomers are identified by the following absorptions:

Natural rubber and Neoprene are distinguished from all other classes by a broad band at 12 mu, and are differentiated from one another by the exact position of this band, by the 7.25 mu band in natural rubber, by the strength and position of the 6.0 mu band, and by the appearance of the 9 mu region. Butyl (GR-I) rubber is distinguished by a strong unique band at 8.13 mu and by a strong doublet at 7.20, 7.30 mu. Nitrile rubbers (Chemigum, Hycar, Perbunan) and Buna-S (GR-S) are characterized by strong bands at 10.3 and 10.9 mu (common to butadiene polymers), and Buna-S is readily identified by unique bands at 6.23, 6.70, and 14.3 mu, while nitrile rubbers are identified by a band at 4.47 mu. Thiokol-FA and Thiokol-ST possess identical spectra, characterized by a unique envelope of strong bands at 8.36, 8.64, 8.98, 9.32, and 968 mu. Thiokol-RD possesses typical nitrile rubber bands at 4.47, 10.25, and 10.86 mu, but is readily set apart by a strong band at 5.86 mu and by a doublet at 7.25, 7.38 mu.

Thus identification of a rubber specimen containing a single elastomer is always possible simply by empirical comparison of the spectrum with reference spectra, such as those of Figures 2 and 4.

For mixtures of elastomers, the ease of qualitative analysis depends on the degree of differences existing in the spectra of the components. For example, less than 1 per cent of a nitrile copolymer may be identified in any mixture by absorption at 4.47 mu, since all other elastomers are highly transparent in this region. Less than 5 per cent of Thiokol-FA can be detected in any mixture by its characteristic bands in the region of 7.5 to 10.5 mu, since these bands, though not isolated, are much stronger than those of other elastomers in this region. Since blends of more than two components are seldom encountered in commercial products, it is generally possible to identifying any component which exists in 5 per cent, or greater, concentration. The limit of detection of Neoprene in natural rubber, however, is probably nearer 10 per cent, since great spectral similarity exists for these elastomers. The major component(s) is best identified by examining a film which transmits about 10 to 20 per cent at 6.8 mu. Thicker films may then be examined over selected wave-length regions to establish the presence or absence of minor components.

Exact spectral correspondence may not always be found for some elastomers because of differences in component proportions and modes of addition in copolymers or oxidation of the sample. These differences do not hinder the analysis and, in addition, furnish valuable information if interpreted in terms of molecular structure. Thus, the relative intensity of the 4.47 mu nitrile absorption distinguishes between high- and low-nitrile copolymers, and emulsion polymers can be differentiated from sodium polymers, since the former are

predominantly 1,4-addition, with absorption at 10.35 mu, while the latter are predominantly 1,2-addition, with absorption at 10.95 mu.

QUANTITATIVE ANALYSIS OF NATURAL-GR-S MIXTURES

Basis of method.—Quantitative spectral analysis of a binary mixture generally involves: (1) selection of a spectroscopic measurement or function which is sensitive to the composition; (2) construction of a working curve expressing the relationship between the spectroscopic function and sample composition for a set of accurately known mixtures; and (3) subsequent analysis of samples by applying analogous measurements to this working curve. The working curve method requires the utmost in experimental reproducibility of the overall procedure, and the results obtained with uncured and cured elastomers show the methods presented to be fully adequate in this respect. The analytical problem relates, therefore, largely to determining the most satisfactory spectroscopic function for the particular analysis. The case of natural-GR-S mixtures is considered here, but since similar spectral differences exist for other binary mixtures analogous procedures and similar results may be obtained in other cases.

Comparison of the spectra of natural rubber and GR-S indicates that the former can be detected in the mixture by methyl absorption at 7.25 mu or by 11.95 mu absorption due to the isoprene structure —$(CH_3)C{=}CH$—, and that the latter can be detected by the 6.70 mu phenyl absorption or by butadiene absorptions at 10.35 and 10.95 mu due to 1,4- and 1,2-addition, respectively. The 7.25 and 6.70 mu bands appear most suitable for natural rubber and GR-S determinations, since both are independent of olefinic bonds which might be expected to change under certain conditions, *e.g.*, with vulcanization, molecular weight, and mode of addition. Since the styrene content of GR-S is maintained as nearly constant as possible by all manufacturers, the number of phenyl and methyl groups present, and hence the intensities of their absorptions, are proportional to the GR-S and natural rubber contents, respectively, of the mixture. The use of the shorter wave-length bands avoids any effects due to variable background absorption at longer wave lengths.

The spectroscopic function to be employed generally includes the transmittance, T, of the sample as the experimentally measured quantity. This is usually expressed in terms of extinction, E, by the equations:

$$E \equiv \log_{10}(1/T) = \log_{10}(I_0/I) = KCt$$

where I_0 and I represent the energy transmitted by the blank and sample, respectively, K is a proportionality constant, C is the concentration, and t is the sample thickness. Any measurement of C is limited in accuracy by the control possible over t and this problem is particularly difficult in case of solid films.

Since it is impractical, if not impossible, to measure or control the thickness of rubber films with sufficient accuracy, it is convenient to eliminate t from the spectroscopic function. This can be done by employing the ratio of extinctions determined at different wave lengths, since only t is independent of wave length. It would be convenient, then, to employ as the spectroscopic function the ratio $E^{7.25}/E^{6.70}$ where the superscripts refer to wave length. In practice, however, this ratio can be determined accurately only for mixtures which contain appreciable constructions of both components, for only under these conditions is it possible to spread a film of given thickness which yields transmittance

values in the accurately measurable range of 20 to 65 per cent at each wave length. This difficulty may be resolved by selecting, as an internal standard, a third band common to both components and of such intensity that the transmittance, both at the internal standard wave length and at the analytical wave length of the minor component, always falls within the accurately measurable range. For this purpose the common band of medium strength at 7.60 mu is especially well suited, since it occurs in both natural rubber and GR-S at so nearly the same intensity as to be almost independent of the composition of the blend. The extinction ratios $E^{6.70}/E^{7.60}$ and $E^{7.25}/E^{7.60}$ thus may be used as functions only of composition to determine GR-S and natural rubber, respectively, and together enable analysis of all mixtures from 0 to 100 per cent. Both ratios are linear with composition over the useful range (see Figure 5).

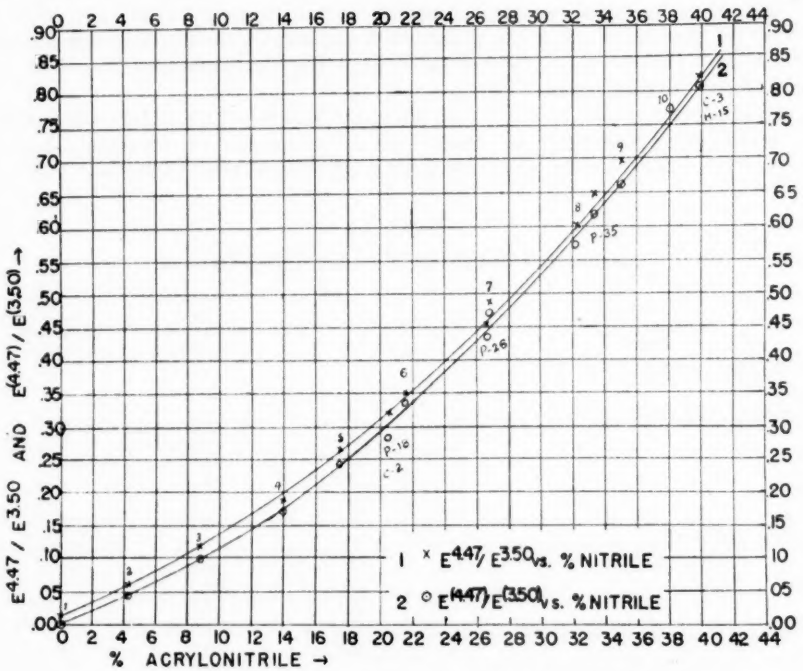


FIG. 5 — CALIBRATION FOR NITRILE DETERMINATION

FIG. 5.—Calibration for nitrile determination.

Analytical procedure.—The following method is presented for the routine analysis of finished rubber articles composed of natural rubber and GR-S. The procedures are in no way exacting, and the time requirement is about 6 man-hours per sample.

Preparation of sample.—A 4-gram sample, which has been milled to pass a No. 20 screen, is extracted for 24 hours with two 80-cc. portions of a 32-68 blend of acetone-chloroform. The extracted sample is completely dissolved in 250 cc. of distilled *o*-dichlorobenzene by refluxing for 24 hours, and the solution is diluted to 300 cc. with benzene. Carbon blacks are removed by Celite filtration, and mineral fillers, if present, by centrifugation. A thick mucilage

for film spreading is obtained by vacuum distillation of the solvent, and films are spread on sodium chloride or potassium bromide plates. If the sample is fairly viscous, the films can be checked for thickness immediately (since *o*-dichlorobenzene is transparent at this wave length) by measurement at 7.60 mu where the transmittance should be between 40 and 60 per cent. After adjustment to an appropriate thickness, the film is dried 40 minutes in a vacuum oven at 80° C, or for 4 hours at room temperature before analytical measurements are made. Films of decided irregularity must not be used.

Measurements and calculations.—Percentage transmittance of each film is measured at 7.60, 7.25, and 6.70 mu. Care must be taken to measure at the center of the bands. Duplicate films and measurements are recommended for accuracy, and transmittance values outside the range 20 to 65 per cent are not used. The extinction ratio $E^{7.25}/E^{7.60}$ or $E^{6.70}/E^{7.60}$ (or both) is obtained, depending on the suitability of the measurements, and plotted against composition for a series of standard mixtures. Subsequent samples are analyzed by the converse procedure of applying the measured ratios to the appropriate working curve.

Experimental results.—Work with standard blends.—The analytical method was tested by applying it to eleven standard samples of accurately known composition. These were made by curing appropriate mixtures (see Table I)

TABLE I

ANALYSIS OF STANDARD NATURAL–GR-S BLENDS

Sample[a] Blend	No.	Natural rubber analysis[c] (per cent)	GR-S analysis[d] (per cent)
F-620 (100% GR-S)	1	00.0	[e]
	2	00.0	[e]
1 (90% GR-S) (10% natural rubber)	1	10.5	[e]
	2	9.5	[e]
	3a	10.5	[e]
	3b	10.5	[e]
	3c	10.7	[e]
	3d	10.7	[e]
2 (80% GR-S) (20% natural rubber)	1	20.0	[e]
	2	21.5	[e]
	3a	19.0	[e]
	3b	19.5	[e]
	3c	19.0	[e]
	3d	20.5	[e]
3 (70% GR-S) (30% natural rubber)	1	31.0	72.0
	2	—	69.0
	3a	29.0	71.5
	3b	31.5	73.0
	3c	30.5	—
	3d	31.7	69.0
4 (60% GR-S) (40% natural rubber)	1	—	60.0
	2	—	60.0
	3a	40.0	—
	3b	—	63.0
	3c	40.5	61.0
	3d	—	59.0

[a] Numbers refer to sample preparation; letters indicate several films measured.
[c] Using curve 2 of Figure 4.
[d] Using curve 1 of Figure 4.
[e] Extinction ratio (though measurable) beyond linear range of working curve.
— Absorption too great for accurate measurement.
[f] Preparations 1 and 2 of blend 7 ruined before preparation of the film.

TABLE I—*Continued*

Sample[a] Blend	No.	Natural rubber analysis[c] (per cent)	GR-S analysis[f] (per cent)
5 (50% GR-S) (50% natural rubber)	1	—	47.5
	2	—	48.5
	3a	—	48.0
	3b	—	52.0
	3c	45.0	50.0
	3d	48.0	52.0
	3e	—	50.5
6 (40% GR-S) (60% natural rubber)	1	—	40.0
	2	—	40.0
	3a	—	41.0
	3b	—	40.5
	3c	—	40.5
	3d	—	39.5
7[f] (30% GR-S) (70% natural rubber)	3a	—	31.0
	3b	—	32.5
	3c	—	30.0
	3d	—	31.0
	4a	—	33.0
	4b	—	32.0
8 (20% GR-S) (80% natural rubber)	1	—	18.0
	2	—	18.5
	3a	—	21.0
	3b	—	21 5
	3c	—	18.2
	3d	—	19.5
9 (10% GR-S) (90% natural rubber)	1	—	09.5
	2	—	10.5
	3a	—	08.5
	3b	—	10.0
	3c	—	08.5
	3d	—	09.5
	3e	—	08.0
F-10 (100% natural rubber)	1	—	00.5
	2	—	02.0

of two master batches of natural and GR-S, compounded with 30 per cent of carbon black. Samples were prepared in triplicate, and several films of each preparation were studied. The analytical results, presented in Table I, were obtained by plotting the measured extinction ratios against the known composition of each sample, and applying the corresponding values to the working curve (Figure 5) drawn through the average value of each group of points. For each blend the several analyses differ from the average only rarely by more than 2 per cent and the average deviation for the 58 results is 1 per cent. The reproducibility of the analytical values for the three separate preparations of each sample is equal to that obtained for duplicate films of any one preparation. This proves conclusively on the one hand the adequacy of the preparation method and shows on the other hand the importance of the quality of the films.

Some films were perfectly smooth, others were somewhat uneven, and this probably accounts for what little variation was obtained. For evaluation of the ratio method of eliminating the effect of film thickness a number of films of greatly different thicknesses were purposely studied, although fairly close control of thickness was easily possible. Despite threefold differences in the 7.60 mu extinction, the analytical results proved without exception to be independent of this factor. Finally, the reproducibility is the same for all concentrations on the linear portion of the working curve. In view of the facts that

these results include all data obtained in development of the method, and that no exceptional degree of regulation was used in any steps of the analysis, it is considered that a quantitative accuracy expressed by an average deviation of 1 per cent is generally obtainable in application of the method to mixtures of high-quality natural rubber-GR-S stocks.

Analysis of mixtures containing reclaim.—The analyses of the standard samples described above were carried out under favorably chosen conditions so that limitations pertaining solely to the experimental procedure could be established. The general usefulness of the method depends, however, on the consistency of the analytical results when stocks of different origin are encountered. Although different stocks exhibit the same general spectral features, slight quantitative differences in polymer structure may produce corresponding differences in band intensities which affect the analytical results.

To determine the maximum effect which would be encountered, attention was directed toward natural rubber-GR-S blends containing a natural-rubber reclaim stock. A different GR-S stock was not studied, since little variation in GR-S would be expected. Six blends containing reclaim, made by curing appropriate mixtures of natural rubber, GR-S, and a tube reclaim, were ex-

TABLE II

ANALYSIS OF RECLAIM-CONTAINING MIXTURES

Sample[a] Blend	No.	Natural rubber analysis[c] (per cent)	GR-S analysis[d] (per cent)
F-10 (100% natural rubber)	1a	—	01.0
	1b	—	—
	2a	—	02.0
	2b	—	—
F-10-4 (50% natural rubber) (50% reclaim)	1a	—	02.5
	1b	•	03.5
	2a	—	05.0
	2b	—	05.5
F-10-1 (100% reclaim)	1a	—	04.0
	1b	54.0	06.0
	2a	—	15.0
	2b	36.0	18.0
	3	47.0	13.0
	4	54.0	14.5
F-10-2 (33.3% natural rubber) (33.3% reclaim) (33.3% GR-S)	1a	—	30.5
	1b	40.0	28.5
	2a	—	33.5
	2b	49.0	33.0
	3	52.0	35.5
F-10-5 (25% natural rubber) (25% reclaim) (50% GR-S)	1a	38.5	45.5
	1b	38.0	46.5
F-10-3 (50% reclaim) (50% GR-S)	1a	30.0	43.0
	1b	32.0	43.0
	2	32.0	47.0
	3	35.0	50.5
F-10-6 (15% natural rubber) (15% reclaim) (70% GR-S)	1a	26.5	69.0
	1b	26.5	70.0
F-620 (100% GR-S)	1a	01.0	•
	1b	01.5	•
	2	03.0	•

[a] Numbers refer to sample preparations; letters indicate several films measured.
[c] Using curve 2 of Figure 4.
[d] Using curve 1 for Figure 4.
• Extinction ratios (though measurable) beyond linear range of working curve.

amined. Several preparations and analyses of each of these samples were made (see Table II), using the previous working curves (Figure V). Although no apparent difficulties were encountered in sample preparation, both the reproducibility and the correctness of the results are much inferior to the accuracy previously reported. The errors are roughly proportional to the reclaim content, and far greater interference is found in the natural rubber (plus reclaim) determination than in the GR-S determination.

For GR-S concentrations of 10 to 70 per cent, an accuracy of ±5 per cent or better can be obtained by using the GR-S working curve and determining natural by difference. For other compositions, as much as 10 per cent error may be obtained. However, if it is assumed that reclaim is always used with at least equal quantities of natural rubber, the overall accuracy of the method may be put at ±5 per cent for mixtures containing reclaim. The seriousness of interference by reclaim is minimized somewhat by the fact that the presence of reclaim can be recognized in important cases. In the absence of reclaim both natural and GR-S can be measured directly only for concentrations near 50 per cent, and in these cases the concentrations total 100 per cent within the limits of error. However, when reclaim is present in sufficient quantity to cause serious interference, it becomes possible to determine both components through a much wider range, and in every case the interference is indicated by a corresponding deviation of total concentration from 100 per cent.

Although the results obtained with blends containing reclaim were not unreasonably erroneous considering the severity of the test, an attempt to obtain more satisfactory results was made by employing a different choice of analytical wave lengths. Results based on measurements at the 11.95 mu absorption of natural rubber were found unreliable, and other procedures employing the functions $E^{10.35}/E^{10.70}$, $E^{10.35}/E^{11.40}$, and $E^{10.95}/E^{11.40}$ yielded satisfactory results for high-quality stocks but no improvement in results for mixtures containing reclaim. The original method appears, therefore, to yield the best accuracy for infrared analysis of natural rubber-GR-S mixtures.

DETERMINATION OF ACRYLONITRILE IN NITRILE COPOLYMERS

Basis of method.—The general procedure described for the spectral analysis of elastomer mixtures can also be used to determine the structural units comprising a given elastomer. Determination of the nitrile (nitrile and acrylonitrile are used interchangeably throughout the discussion) content of nitrile copolymers is considered in detail, but similar methods may readily be developed for analogous problems, such as determination of the styrene content of Buna-S or the ratio of 1,2- to 1,4-addition structures in polybutadienes.

Satisfactory procedures for sample preparation of cured and uncured nitrile copolymers have been presented, so only the spectroscopic function need be considered. The $E^{4.47}/E^{3.50}$ ratio obtained by measuring the transmittance at the 4.47 mu nitrile band (due to the C≡N valence vibration) and at the 3.50 mu C—H absorption, is a satisfactory function and can be determined accurately for samples containing 0 to 50 per cent of nitrile, which range includes all nitrile rubbers of industrial importance. A working curve is constructed by plotting the spectroscopic function versus composition for a series of standard samples, and subsequent analyses are made by applying analogous measurements to the curve.

If the transmittance is measured relative to a blank plate at the analytical wave lengths, an error due to reflection and scattering losses in the sample film results, and the calibration curve does not read zero at 0 per cent nitrile

(pure polybutadiene). Although this effect is scarcely noticeable for nitrile concentrations above 15 per cent, it gives appreciable positive errors at low nitrile concentrations. These errors may be eliminated entirely by choosing as "100 per cent transmittance" the transmittance of the sample film itself at a nearby wave length of maximum transmittance, *i.e.*, at 4.60 mu, rather than the transmittance of a blank plate at the analytical wave length. With this modification polybutadiene shows 0 per cent absorption at 4.47 mu, and valid results are obtained for low nitrile samples, irrespective of wide variations in the general transparency of the films.

Analytical procedure. Sample preparation.—For gum rubber, a 2-gram sample is cut into thin strips and extracted for 24 hours with two 80-cc. portions of 85 per cent ethanol. The extracted sample is allowed to soften and swell in 100 cc. of ethylene dichloride for 2 hours and then thoroughly mixed in a Waring Blendor. Excess solvent is removed by evaporation on an A.S.T.M. gum bath at 70° C, but evaporation must be stopped before gelling occurs. For cured rubber, a 4-gram sample, which has been milled to pass a No. 20

TABLE III

ACRYLONITRILE ANALYSIS OF COMMERCIAL BUNA-N COPOLYMERS

Sample Copolymer[c]	Set[d] and run	Nitrile determination (%)[b] Uncorrected	Corrected
Perbunan-10	1a	07.2	08.2
	b	09.4	08.8
Perbunan-16	1a	14.0	14.8
	b	13.6	14.6
Perbunan-18	1a	19.6	—
(20.5%)	b	20.0	—
	c	19.6	—
	2a	18.6	19.0
	b	19.5	19.5
	3a	20.6	—
	b	20.4	—
	c	20.2	18.4
Perbunan-26	1a	26.2	—
(26.7%)	b	26.4	—
	c	25.2	—
	d	26.2	—
	2a	26.4	26.6
	b	27.8	27.7
	3a	25.4	—
	b	26.4	—
	c	25.6	—
Perbunan-35	1a	34.6	—
(33.5%)	b	34.8	—
	c	34.4	—
	2a	37.6	34.2
	b	37.4	34.5
	3a[e]	34.8	—
	b	34.4	—
	c	34.2	31.2

[b] Using appropriate working curve of Figure 5.
[c] Nitrile content as determined by Kjeldahl analysis given in parentheses.
[d] Numbers refer to sample preparations; letters designate several films studied. Preparations 1, 2 are of gum samples; preparation 3 is cured and compounded samples.
[e] Gelatinous sample and correspondingly unsatisfactory films.

TABLE III—*Continued*

Sample Copolymer[c]	Set[d] and run	Nitrile determination (%)[b] Uncorrected	Corrected
Chemigum-N-1 (30.8%)	1a	30.6	—
	b	30.4	—
	c	30.8	—
	2a	29.6	29.2
	b	29.2	28.8
	3a	31.0	—
	b	31.2	—
	c	30.6	29.4
Chemigum-N-2 (20.7%)	1a	19.2	—
	b	21.0	—
	c	19.8	—
	2a	18.2	19.0
	b	20.1	19.5
	3a	20.6	—
	b	20.8	—
	c	20.0	18.4
Chemigum-N-3 (40.0%)	1a	39.0	—
	b	39.8	—
	2a	41.0	40.6
	b	41.7	41.2
	3a	39.8	—
	b	40.8	—
	c	41.0	41.0
Hycar OR-15 (41.8%)	1a	39.2	—
	b	39.8	—
	c	41.0	—
	2a	41.0	40.8
	b	42.3	41.7
	3a	40.0	—
	b	40.8	—
	c	39.8	39.4
Hycar OR-25 (33.0%)	1a	30.4	—
	b	31.0	—
	c	31.0	—
	2a	32.0	31.2
	b	32.6	31.5
	3a	30.6	—
	b	31.4	—
	c	31.2	29.2

screen, is extracted for 24 hours with two 80-cc. portions of a 32–68 blend of acetone-chloroform. The extracted sample is dissolved in 300 cc. of distilled *o*-dichlorobenzene under reflux, the solvent being used successively in two portions, and blendorization being employed if necessary. Carbon blacks are removed by Celite filtration, and mineral fillers by centrifugation. Vacuum distillation is employed for solvent removal. Films are spread on sodium chloride or potassium bromide plates, and the residual solvent is removed by evaporation at room temperature or more rapidly in a vacuum oven at 80° C.

Spectroscopic measurements.—Percentage transmittance of each film relative to a blank plate is measured at 4.60, 4.47, and 3.50 mu, care being taken to locate the maxima of the bands (except at 4.60 mu). Films of satisfactory thickness give about 20 to 25 per cent transmittance at 3.50 mu. The percentage transmitances at 3.50 and 4.47 mu are corrected for film scattering by dividing by the decimal transmittance at 4.60 mu and the extinction ratio $E^{(4.47)}/E^{(3.50)}$ is calculated, parentheses being used to denote the use of cor-

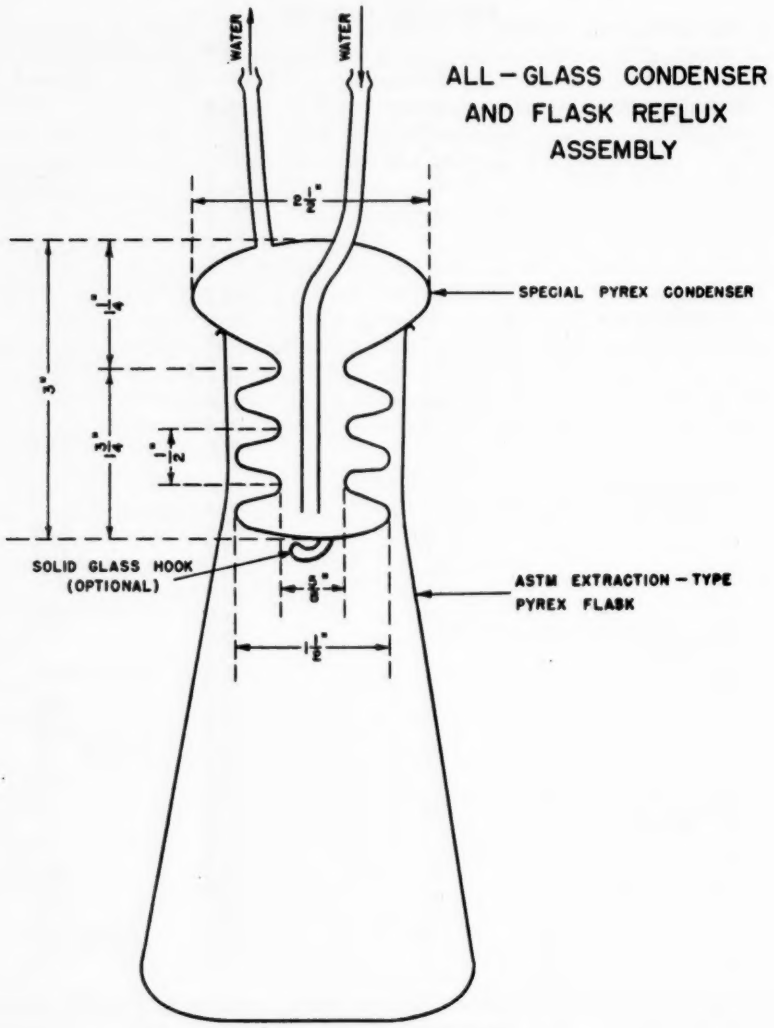


FIG. 6.—All-glass reflux assembly.

rected transmittance values. This ratio is plotted *versus* composition for several known samples, and subsequent samples are analyzed by the converse procedure of applying the measured ratios to this curve. Films and measurements are made in duplicate as a check on accuracy.

Experimental results.—The analytical method was tested by applying it to over fifty samples prepared from a variety of nitrile copolymers. Preliminary measurements were made on gum samples of Perbunan-18, Perbunan-26, and Perbunan-35, Chemigum-N-1, N-2, and N-3, and Hycar-OR-15 and OR-25. A working curve was constructed using the average values of the uncorrected analytical function, and the nitrile values were determined by Kjeldahl analysis (total nitrogen assumed to be nitrile nitrogen). All values were then applied to the working curve, and the results are presented as set 1 in Table III.

Despite neglect of the scattering correction and the use of films of widely different quality and thickness, the analytical results show a mean deviation of ±1 per cent and a maximum error only rarely twice this value. The error is in no sense consistent with film thickness, and can be attributed entirely to differences in film quality. The overall method was then critically tested by using the same working curve to analyze a set of the same nitrile copolymer stocks which had been compounded with carbon black and cured. The agreement of the results (set 3, Table III) with those for gum samples is fully

TABLE IV

ACRYLONITRILE ANALYSIS OF SPECIAL NITRILE COPOLYMERS

Sample Copolymer[c]	Set[d] and run	Nitrile determination (%)[b]	
		Uncorrected	Corrected
1 (0.9%)	1a	04.8	0.0
	b	02.4	0.0
	2a	00.0	0.0
	b	00.0	0.0
2 (4.2%)	1a	04.0	4.4
	1b	03.6	4.2
	2a	03.2	4.0
	2b	03.2	4.0
3 (8.7%)	1a	08.8	9.2
	1b	08.2	8.6
	2a	07.8	8.8
4 (14.0%)	1a	12.8	13.6
	1b	12.8	13.8
	2a	12.6	13.8
	2b	12.6	13.6
5 (17.0%)	1a	18.0	17.4
	2a	17.6	17.8
	2b	17.6	18.0
6 (21.7%)	1a	23.0	23.2
	1b	21.6	22.0
	2a	21.8	22.0
	2b	22.2	22.4
7 (27.0%)	1a	28.8	28.2
	2a	27.8	27.6
	2b	29.0	28.0
8 (32.3%)	1a	34.6	33.6
	2a	32.8	31.8
	2b	32.4	31.4
9[e] (35.2%)	1a	41.2	38.6
	1b	42.8	38.4
	2a	38.6	35.0
10 (38.2%)	1a	40.0	39.2
	1b	40.0	39.0
	1c	40.4	38.6
	1d	40.8	38.8

[b] Using appropriate working curve of Figure 5.
[c] Nitrile content as determined by Kjeldahl analysis given in parentheses.
[d] Numbers refer to sample preparations; letters designate several films studied. Both preparations are of gum samples.
[e] Gelatinous sample and correspondingly unsatisfactory films.

as close as the reproducibility obtained in either set for duplicate films of the same preparation. This severe test of the overall method shows its complete reliability on the one hand and the importance of obtaining high-quality films on the other.

For extension of the calibration below 20 per cent nitrile, a specially prepared set of ten nitrile-copolymer gum elastomers (supplied by the Firestone Tire & Rubber Company) covering the range 0 to 40 per cent nitrile were prepared in duplicate and several films of each preparation were measured at 3.50, 4.47, and 4.60 mu. Extinction ratios were calculated both with and without correction for scattering, and the average values for each sample were plotted *versus* nitrile values based on the manufacturer's Kjeldahl analyses to obtain the working curves shown in Figure 6. Curve 1 (uncorrected ratios) was identical with that previously obtained for the commercial elastomers and established the equivalence both of the spectral results and of the chemical analyses for both series of samples. The analytical results obtained by applying the ratios for each film to the proper curve of Figure 6 are presented in Table IV. For each curve an average deviation of ± 1 per cent was obtained for samples containing 15 per cent or more nitrile; for samples of less than 15 per cent nitrile, no decrease in accuracy resulted when the corrected ratio was used (curve 2), whereas the uncorrected ratio gave considerable error. The errors were independent of film thickness and are attributable entirely to differences in the quality of the films. Some films obtained from gelatinous preparations were of such low transparency that scattering losses contributed half of the measured "absorption". Even with such inferior films, the use of the scattering correction gave results within about 2 per cent of the correct value.

In view of the superior reliability of the corrected function, the analysis of both the cured and uncured samples of the eight commercial nitrile rubbers was repeated, using both corrected and uncorrected measurements. The accuracy of the results (set 2, Table III) corresponds to ± 1 per cent average error for either function, except for Perbunan-35, where extreme gelation caused large errors in the results, without scattering corrected function. Since normally only the corrected functions would be employed in analysis, it appears established that an average deviation of ± 1 per cent is readily obtainable when this method is used, to determine the nitrile content of either raw or cured nitrile copolymers.

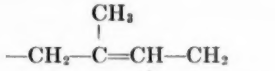
SPECTRAL–STRUCTURAL RELATIONSHIPS

It remains impossible to assign many of the bands in the spectra of polyatomic molecules to exact molecular vibrations. However, certain functional groups in the molecule frequently control certain vibrations, and thus it is possible in many cases to correlate spectral absorption with molecular structure. In the case of rubber spectra, these relationships are incomplete and are mostly empirical, but because of their importance in connection with analytical work, as well as in the general elucidation of molecular structure, some of the correlations which have been found useful in this investigation are summarized here.

Bands due to C—H vibrations are found in the spectra of all hydrocarbon-type elastomers, and these may be considered collectively before passing on to those which characterize the various elastomers. The bands in the neighborhood of 3.4 mu are due chiefly to C—H valency (stretch) vibrations, while

those at 7 mu are due to C—H deformation (bending) vibrations. The study of a large number of hydrocarbons has shown that $-CH_3$, methyl, groups absorb at 3.37 mu and at 7.25 mu while $>CH_2$, methylene, groups absorb at 3.42 mu, and that both methyl and methylene groups absorb at 3.5 mu and in the 6.81 to 6.98 mu region. Greater spectral resolution has shown that the absorption in the 3.4 mu region is complex[9] and the presence of additional unresolved bands determines the exact contour of the bands obtained here and confuses the assignment. However, the correlations obtained under moderate resolution agree with the frequencies assigned to the stronger C—H bands by Fox and Martin[9] and are useful in identifying the various types of C—H bands when they are present in significant proportions and in not too great variety. These bands in Figures 2 and 4 are too strong to show the resolvable structure, but results obtained with thinner films were consistent with expected absorptions for all of the elastomers, except for a minor difference in the case of Butyl, where a band at 3.50 mu was expected but not found. Two additional bands at 3.67 and 2.32 mu are found in the spectra of most elastomers, as well as in the spectra of most hydrocarbons, and are due to combinations or harmonics of other C—H frequencies.

Natural (Hevea) rubber consists of long chainlike molecules composed of the recurring isoprene unit, I, and all the strong bands in the spectrum are consistent with this structure.



(I)

Wave length (Mu)	Absorbing structure
3.37	$-CH_3$
3.42	$>CH_2$
3.50	$-CH_3$, $>CH_2$
6.00	C=C (valency vibration)
6.90	$-CH_3$, $>CH_2$
7.25	$-CH_3$
11.95	$-C(CH_3)=CH-$

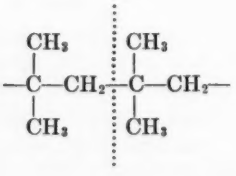
Sheppard and Sutherland[3] suggest that weak absorption around 3 mu is composed of a band at 3.1 which is to be distinguished from hydroxyl (oxidation) absorption at 3.0 mu. Increased resolution obtained here has located this band at 3.05 mu, while the oxidation impurity absorption (which always appears stronger in vulcanized and reclaimed samples) appears to be nearer 2.9 mu. The 3.05 mu band has previously been assigned[3] either to a combination frequency or to the fundamental of the hydrogen vibration relative to a tertiary carbon, but it is undoubtedly due to an impurity absorption, since it does not appear in the spectra of deproteinized samples[10]. The same authors also report a new band at 4.98 mu which has not been confirmed here. This band was found for only one sample, and apparently originates in an impurity. However, most hydrocarbons absorb weakly in this region and under proper conditions, *i.e.*, using a thick film, a band at 4.93 mu would be expected in the spectrum of natural rubber. All other bands reported by Sheppard and Sutherland were also found in this investigation.

Weak bands in the region of 5.8 mu are due to C=O carbonyl oxygen resulting from oxidation, and, as for the 2.9 mu hydroxyl absorption, these

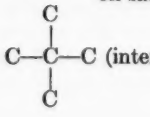
impurity bands are stronger in vulcanizates than in raw rubbers. The 6 mu olefinic absorption varies with structure, terminal linkages (vinyl groups) absorbing at 6.10 mu, internal double bonds absorbing at slightly shorter wave lengths and in general at much less intensity, and double bonds at branching centers usually absorbing at slightly different wave lengths than the corresponding unbranched structures. The olefinic absorption for the normal rubber skeleton absorbs at exactly 6.00 mu, and the weaker absorption at approximately 6.1 mu probably results from olefinic groups modified by removal from methyl branching centers or by proximity to the end of the polymer chain. Absorption around 6.5 mu found by Barnes[11], but not by Sheppard and Sutherland[3], was not consistent in the various samples and must be due to an impurity.

For natural rubber, as for the other elastomers, the bands beyond 7.5 mu are generally characteristic of larger molecular groupings, so that correlations which have been found for liquid hydrocarbons are not necessarily applicable to rubber spectra, since considerable variation in position and intensity of absorption occurs with change of state. However, the strong band at 11.95 mu has been assigned by Thompson and Torkington[2] to type $R_1R_2C{=}CHR_3$ structures and this corresponds to structure I for natural rubber, provided that R_1 or R_2 is methyl. Since the bands which characterize other olefinic structures such as those in IV and V (see below) are absent all double bonds in natural rubber apparently occur at branching position. The question of *cis-trans*-isomerism about the double bond[12] is being considered, but must be deferred for the present.

Butyl rubber (GR-I) designates a class of elastomers prepared by low-temperature copolymerization of isobutylene with a very small percentage of a diolefin, *e.g.*, isoprene. The elastomer chains undoubtedly consist chiefly of head-to-tail polyisobutylene units, II, separated occasionally by a 1,4-addition isoprene unit, I. The small olefin content (about 0.6 mole-per cent) contributes the necessary property of vulcanizability, but does not contribute significantly to the absorption, so that the spectrum of GR-I corresponds to that of pure head-to-tail polyisobutylene[2], and all the strong bands correlate entirely with structure II.

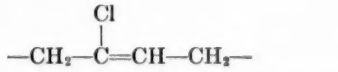


II

Wave length (mu)	Absorbing structure
ca. 3.40	$-CH_3$, $>CH_2$
6.80	$-CH_3$, $>CH_2$
7.20, 7.30	$-CH_3$ (deformation vibration; two methyls on same carbon atom)
8.13	 (internal quaternary carbon atom)
8.56	
10.52	
10.82	

In some cases the 3.4 mu absorption was resolved into methyl and methylene bands at 3.38 and 3.44 mu, but the bands are diffuse and difficult to resolve. A band ordinarily found at 3.50 mu is missing, which indicates that the absorption in this region probably consists of several unresolved bands. Interpretation of the bands at 8.56, 10.52, and 10.82 is uncertain, but their origin certainly lies in distortion vibrations of the carbon skeleton[2]. A quaternary carbon atom does not seem to be fundamentally related to these bands; however, 1,1,6-triisobutylhexane, 1,1,2-triisobutylethane, 1,1-diisobutyltridecane, and isobutylbenzene all absorb at 8.55, 10.55, and 10.85 mu (but not at 8.0 to 8.3 mu), whereas isopropylbenzene absorbs only at 10.85 mu.

Neoprene is a trade-name which designates a variety of elastomers formed by polymerization of chloroprene which are composed of the recurring structure III, which differs from I only in that the methyl has been replaced by chlorine. Accordingly, the spectrum of Neoprene agrees with that of natural rubber if allowance is made for the expected effects of chlorine substitution.



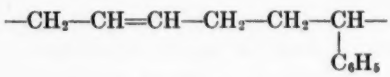
III

Wave length (mu)	Absorbing structure
3.42	>CH₂
3.50	>CH₂
6.02	C=C
6.90, 6.98	>CH₂
8.92	
12.10	—C(Cl)=CH—

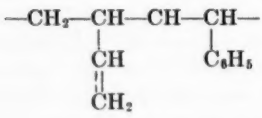
An unresolved band at 3.30 mu is probably due to a fundamental vibration of hydrogen relative to a tertiary carbon[9], and the 3.38 mu methyl band is absent. Oxidation impurity bands at 2.90 mu and from 5.5 to 6.0 mu are generally present, especially in cured samples. The 6.02 mu band with a shoulder at 6.12 mu is analogous to a similar band in the spectrum of natural rubber, and is correlated with the olefinic structure, although Sears[13] suggests that a harmonic of the 12.10 mu band may contribute here too. The 6.90 mu band is the usual C—H deformation and the 6.98 mu band has a similar origin, the shift resulting from chlorine substitution[2] on adjacent carbon atoms. Other reproducible bands are found at 7.42, 7.66, 8.16, 8.94, 9.20, and 10.00 mu, that at 8.94 being one of the most distinctive features of the Neoprene spectrum (for analytical purposes). Sears[13] suggests that the weak absorption at 12.85 mu may be due to C—Cl absorption. There seem to be no strong bands between 13 and 20 mu where C—Cl vibrations might be expected.

Neoprene-ILS is a polychloroprene which contains a small proportion of acrylonitrile. Except for the nitrile absorption at 4.47 mu, the spectrum of Neoprene-ILS is virtually identical with that of Neoprene-GN and Neoprene-E.

Buna-S is a generic designation for the copolymers of butadiene with styrene, of which GR-S is the particular product resulting from the emulsion copolymerization of 3 parts of butadiene with 1 part of styrene. Condensation can occur by either 1,4- or 1,2-addition, giving, respectively, the structural units IV and V, both of which are shown by the infrared spectrum.



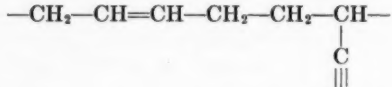
IV



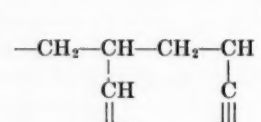
V

Wave length (mu)	Absorbing structure
3.42	$>CH_2$
3.50	$>CH_2$
6.10	$>C=CH_2$
6.23	Phenyl, C_6H_5—
6.70	Phenyl, C_6H_5—
6.88, 6.96	$>CH_2$
10.35	—CH=CH— (1,4-addition)
10.97	$-CH=CH_2$ (1,2-addition)
13.16	Phenyl C_6H_5—
14.28	Phenyl, C_6H_5—

Aromatic C—H absorption, which usually appears as a band or doublet at 3.26 and 3.30 mu, is indicated only by a shoulder in the GR-S spectra and probably is unresolved owing to interference from an additional tertiary C—H band at 3.35 mu. The 6.10 mu band is due to terminal olefinic (vinyl) groups and a weaker band at 6.00 mu is characteristic of internal olefinic linkages. The bands from 7 to 9 mu are definitely reproducible for GR-S, but they have not been interpreted. Thompson and Torkington[2] have shown the strong 10.35 mu band to be associated with the structure $R_1CH=CH_2$, and the 10.97 (and also the weaker band at 10.15) to be associated with the structure $RCH=CH_2$ of a vinyl group, all these bands arising from CH deformation vibrations. The relative intensities of these bands have been used at this laboratory and elsewhere[14] to derive information concerning the relative amounts of 1,4- and 1,2-addition in butadiene polymers, and it is noted that 1,4-addition (structure IV) predominates in GR-S as in other emulsion polymers. The 14.3 mu band is characteristic of all monoalkyl benzenes, and a



VI



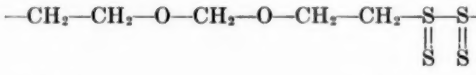
VII

Wave length (mu)	Absorbing structure
3.42	$>CH_2$
3.50	$>CH_2$
4.57	$-C\equiv N$
6.10	$>C=CH_2$
6.90	$>CH_2$
10.32	—CH=CH— (1,4-addition)
10.86	$-CH=CH_2$ (1,2-addition) (vinyl group)

band around 13.2 mu seems to appear whenever the alkyl group differs from the methylene structure at the attachment carbon.

Nitrile rubber is a generic designation for a variety of copolymers, including Hycar-OR, Perbunan, Chemigum, and Butaprene, formed by emulsion copolymerization of butadiene with 15 to 40 per cent of acrylonitrile. Condensation can proceed by either 1,4- or 1,2-addition, giving, respectively, structural unit VI or VII. The spectrum is similar to that of the structurally analogous Buna-S, except that the phenyl bands are all absent and a new nitrile band due to the C≡N valency vibration[15] appears at 4.47 mu.

Thiokol is commonly used to designate elastic resins containing sulfur, and formed by condensation of sodium polysulfide with ethylene dichloride or its derivatives. Thiokol-FA is one variety made by reaction of sodium polysulfide with dichloroethylformal to give the recurring structure VIII.



VIII

Wave length (mu)	Absorbing structure
3.42	>CH_2 (valency)
6.82	>CH_2 (deformation)
7.08	
7.26	
7.82	
8.36	
8.64	
8.98	
9.32	
9.68	
10.53	

As expected, the infrared spectrum bears no great resemblance to the spectra of the common hydrocarbon-type elastomers.

Except for the S—H (thiol) frequency at 3.9 mu, which is not present here, very little is known about the characteristic absorption frequencies of sulfur compounds[3], especially these concerned in structure VIII. The aliphatic ether oxygen groups probably account for the absorption envelope in the 8.5 to 10.5 mu region, but the origins of the discrete maxima are not known.

Thiokol-RD, contrary to the usual terminology, is a nonsulfur material formed by interpolymerization of butadiene, acrylonitrile, and an unsaturated ketone. The molecular units of the interpolymer can hardly be predicted with completeness, but the expected nitrile copolymer structures VI and VII as well as additional ketonic structures are evident from the spectrum.

Wave length (mu)	Absorbing structure
3.42	>CH_2 (aliphatic)
3.50	>CH_2, —CH_3
4.47	—C≡N (nitrile)
5.86	>C=O (carbonyl)
6.00	>C=C< (aliphatic)
6.84 to 6.94	>CH_2 and —CH_3 (deformation)
7.25	—CH_3 (deformation)
7.38	
10.25	—CH=CH— (1,4-addition)
10.86	—CH=CH_2 (1,2-addition) (vinyl group)

The band at 5.86 mu is too strong to be due to oxidation impurities, and must be ascribed to the presence of carbonyl oxygen structures incorporated into the elastomer during polymerization.

ACKNOWLEDGMENT

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REFERENCES

[1] Wright, *Ind. Eng. Chem. Anal. Ed.* **13**, 1 (1941); Gore, *J. Chem. Education* **20**, 223 (1943); Barnes, Gore, Liddel, and Williams, "Infrared Spectroscopy, Industrial Applications and Bibliography", New York, **1944**; Sutherland, Thompson, *et al.*, *Trans. Faraday Soc.* **41**, 171 (1945).
[2] Thompson and Torkington, *Trans. Faraday Soc.* **41**, 246 (1945).
[3] Sheppard and Sutherland, *Trans. Faraday Soc.* **41**, 261 (1945).
[4] Cole and Field, *Ind. Eng. Chem.* **39**, 174 (1947).
[5] Barnes, Williams, Davis and Gieseke, *Ind. Eng. Chem. Anal. Ed.* **16**, 9 (1944).
[6] The Waring Blendor, Cenco No. 17,233, with No. 17,244 (small-size) jar was used.
[7] Nielsen, Crawford, and Smith, *J. Optical Soc. Am.* **37**, 296 (1947).
[8] American Society for Testing Materials, "Tentative Methods of Chemical Analysis of Rubber Products", Standards Supplement, Part III, **1943**, Section D, 297–43T.
[9] Fox and Martin, *Proc. Roy. Soc.* **A175**, 208 (1940).
[10] The results are to be published shortly.
[11] Barnes, Liddel and Williams, *Ind. Eng. Chem. Anal. Ed.* **15**, 83 (1943).
[12] Hendricks, Wildman and Jones, *Arch. Biochem.* **7**, 427 (1945).
[13] Sears, *J. Applied Physics* **12**, 35 (1944).
[14] Field, Woodford and Gehman, *J. Applied Physics* **17**, 386 (1947).
[15] Thompson and Torkington, *J. Chem. Soc.* **11**, 597 (1944).

PROPERTIES OF EBONITE. XXXIV. INFLUENCE OF ORGANIC ACCELERATORS OF VULCANIZATION *

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INTRODUCTION

One of the disadvantages of ebonite is that its production requires a long vulcanizing process, owing to the inherent slowness, at practicable vulcanizing temperatures, of the formation of the hard rubber-sulfur compound. The use of organic accelerators naturally suggests itself as a means of overcoming this difficulty, and it therefore becomes important to know how effectively they speed up the hard rubber reaction and whether they improve or impair the technically important properties of ebonite. Another point requiring investigation is whether accelerators fundamentally alter the course of the rubber-sulfur reaction and the nature of the reaction product, as they appear to do in the formation of soft rubber. This is of more than academic interest, because one troublesome feature of the normal hard rubber reaction is the large evolution of heat; if accelerators could so modify the reaction as to reduce this heat, they would prove very useful.

Although almost every type of organic accelerator has been tried or recommended for use in ebonite, not much systematic quantitative work has been published; the principal papers are listed in the bibliography[1]. Published information shows that organic accelerators are much less active in ebonite than in soft rubber, that different types have not the same relative activities as in the latter, and that the usual metallic oxide activators are comparatively ineffective. It is not clear, however, whether accelerators speed up the hard rubber reaction, whether they enable ebonite to be formed with less than the normal proportion of sulfur, and whether they produce better ebonite.

Experiments have accordingly been made to provide definite evidence on these points, and also to study the effects of organic accelerators and metallic oxide activators on (1) heat evolution during the hard rubber reaction, and the consequent maximum safe rates of vulcanization, and (2) the production of "set-cures".

The importance of (1) lies in the fact that, although an accelerator may speed vulcanization, it does not necessarily enable the vulcanizing period to be shortened. Quicker vulcanization means more rapid heat evolution and hence greater danger of overheating. For every mix, vulcanized as sheets of a given thickness, there is a critical temperature above which overheating becomes excessive, and a corresponding critical vulcanizing rate, which is the maximum rate that can safely be used. The object of the experiments was to find whether this rate could be increased, and hence the vulcanizing period shortened, by using organic accelerators. The method adopted was to vulcanize specimens of standard size in open steam at successively higher temperatures until a "blow-out", *i.e.*, excessive porosity and swelling, occurred through overheating.

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The significance of (2) arises from the observation during this investigation that zinc and magnesium oxides do not activate organic accelerators in the later reaction involved in the formation of ebonite. Nevertheless they may activate the early stages involved in "set-curing" (in moulds) articles that are to be given a final vulcanization in open steam. If this were the case, such activators would be of practical value.

EXPERIMENTAL

Except where otherwise indicated, a 68:32 rubber-sulfur base stock was used; other ingredients (see Table 1) are expressed as parts by weight per 100 parts of base stock. Vulcanization was carried out in moulds in either a platen or autoclave press, and test methods were generally as described in previous reports in this series[2].

ACCELERATION OF VULCANIZATION

This part of the investigation covered accelerators of different types, the influence of activators (zinc and magnesium oxides) on the behavior of each type, and the variation of the proportion of one typical accelerator.

Both the disappearance of free sulfur and the rise in plastic-yield temperature with advancing vulcanization are speeded up by most of the accelerators examined. This is illustrated in Figures 1 and 2, showing the effects of 1.5 parts of four different accelerators, and by the values of the *acceleration factor* (Table 1), expressed as the number of hours' vulcanization (at 155° C) required for the unaccelerated mix to reach the same degree of vulcanization as is

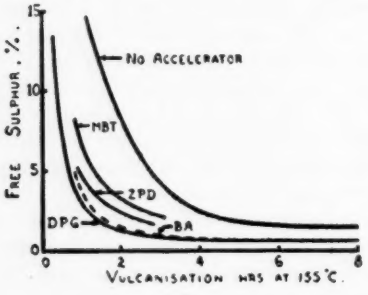

FIG. 1.

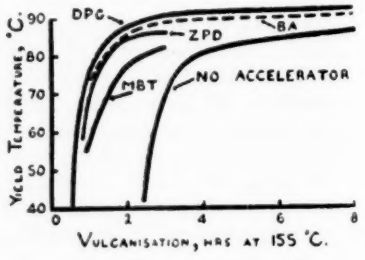

FIG. 2.

TABLE 1

ACCELERATION FACTOR

The H64, H65, and H67 series contain, respectively, no metallic oxide, 5 parts of zinc oxide, and 5 parts of magnesium oxide

Accelerator (1.5 parts)	H64	H65	H67
Diphenylguanidine (DPG)	3.6	1.9	4.0
Crotonaldehyde-aniline (Vulkacit-CT)	3.7	3.1	2.6
Butyraldehyde-aniline (BA)	3.1	2.3	2.8
Zinc pentamethylenedithiocarbamate (ZPD)	2.9	2.6	2.4
Triethyltrimethylenetriamine (trimene base)	2.9	2.0	2.0
Tetraethylthiuram disulfide (TET)	2.8	2.3	2.3
Mercaptobenzothiazole (MBT)	2.4	?	1.9
Hexamethylenetetramine (HMT)	1.3	1.7	*
Lead dimethyldithiocarbamate (LDC)	1.3	1.5	*

* Did not vulcanize to the ebonite stage in 1 hour at 155° C.

reached by the accelerated mix after 1 hour. These values are calculated from free sulfur data; similar values are indicated by the plastic yield temperatures.

Estimates of the relative activities of the different accelerators from the free sulfur and yield temperature data, respectively, agree well with one another, and, in a general way, with published data and statements. They show that DPG is generally the most active, followed by BA and Vulkacit CT, then ZPD and Trimene Base, with MBT still lower, and HMT and LDC at the bottom of the list, being almost ineffective except perhaps in presence of zinc oxide.

Comparison with data for soft rubber provides definite confirmation of two generally accepted points: (1) that organic accelerators are less active in forming hard rubber than soft rubber; for ebonite the highest acceleration factor (in presence of zinc oxide as activator) is about 3, whereas for soft rubber the highest value among the accelerators listed in Table 1 is about 60 (ZPD); (2) the relative activities are not the same in the two cases, although there are certain similarities; the approximate orders, for mixes containing zinc oxide, are:

	Ebonite	Soft rubber
quickest	Vulkacit-CT	ZPD
	ZPD	TET
	BA	BA
	TET	MBT
	Trimene base	Vulkacit-CT
	DPG	Trimene base
	MBT	DPG
slowest	HMT	HMT

(LDC is omitted because in soft rubber it needs litharge for activation.)

The effect of varying the proportion of accelerator was studied with DPG. The test data, particularly for plastic yield temperature, showed that the best results are obtained with about 2.5 parts or rather more:

Parts DPG	1	2.5	5	10
Yield temperature (° C) after vulcanization at				
141° C for: 2 hours	26	55.5	54	46
3 hours	55	75	69.5	60
4 hours	73	83.5	75	68

Presumably the softening effect of resinous decomposition products of the excess accelerator explains the fall in yield temperature with the larger proportions.

It is often stated that organic accelerators are effective only in the early soft rubber stage of vulcanization, and do not promote the hard rubber reaction, although published data[3] suggest the contrary. The present investigation shows this view to be incorrect. Curve I of Figure 3 represents the decrease in free sulfur with advancing vulcanization (at 155° C) of an unaccelerated mix. Curves II, III, and IV relate, respectively, to mixes with 1.0, 1.5, and 5.0 parts of DPG; these are plotted on the same time scale but have been moved horizontally so as to bring their upper ends on to Curve I. In all these accelerated mixes the free sulfur decreases more quickly than in the control mix I, and since Curves II–IV relate to compounds with vulcanization coefficients between 35 and 47, it is clearly the hard rubber reaction that is being accelerated. A study of the corresponding data for yield temperature leads to the same conclusion. These results thus confirm definitely the indications given by previous investigations.

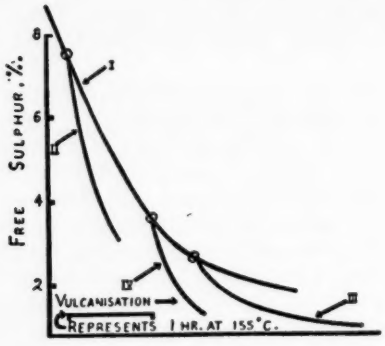

FIG. 3.

An important conclusion from Table 1 is that zinc and magnesium oxides do not enhance the activity of the accelerators, since they usually reduce the acceleration factor. Moreover, the effect of accelerators in raising the yield temperature is not enhanced by either of the oxides. The metallic oxides thus do not behave as true activators of the hard rubber reaction. Hence there would be no point in using them as activators in accelerated ebonite mixes, unless they speed the early (soft rubber) stage and so facilitate set-curing of moulded articles that are to be finally vulcanized in open steam.

Generally the mixes with metallic oxides vulcanize rather more quickly than those without, but this is simply because the oxides are themselves mild accelerators. There are indications, also, that they exert specific effects, since the accelerators do not fall in the same order of activity in the three series of mixes in Table 1.

CRITICAL VULCANIZING RATE

Slabs $6 \times 3 \times \frac{1}{2}$ inch of the mixings shown in Table 2 were given a preliminary moulding in a platen press at 141° C for 60 minutes (blank mixing) or 23 minutes (accelerated mixings), this shorter period corresponding to the increased rate of vulcanization. The edges of the slabs were discarded and the

TABLE 2

ALL MIXES CONTAINED RUBBER 68, SULFUR 32

Series	Accelerator (1.5 parts) and activator (5 parts)	Blow-out temperature (° C)	Relative vulcanizing rate at fixed temperature	Critical vulcanizing rate
I	nil	156	(1.0)	(1.0)
	ZPD	147	2.9	1.35
	TET	147	2.8	1.3
	ZDC	147	2.6–3.4*	1.2–1.6
II	nil	150	(1.0)	(1.0)
	DPG	139	3.7	1.45
	DPG + ZnO	140	2.6	1.1
	DPG + MgO	140	4.5	1.9
	BA	143	3.1	1.7
	BA + ZnO	139	3.1	1.2
	BA + MgO	146	3.6	2.5

* ZDC was not included in Section II. 1; the figures quoted are deduced from work by Davies[5] and Morley[6].

central portions cut into 1-inch squares, which were then embedded in French chalk and vulcanized at various temperatures in open steam. The range of temperatures was adjusted for each mixing so as to cover the region where blow-out first occurred; the blow-out temperature for samples of these dimensions could thus be found. (These temperatures are not valid for specimens of other dimensions, since the exothermic temperature rise in, for instance, a sheet is very dependent on the thickness[4].

In practice an article would never be vulcanized at its blow-out temperature, but it can be assumed that the critical temperature (at which the exothermic temperature rise remains below a predetermined safe limit) always lies at about the same temperature interval below the blow-out temperature. Consequently, differences in critical temperature are the same as differences in blow-out temperature. The critical temperatures alone, however, do not give the required information, and must be translated into the corresponding rates of vulcanization at these temperatures. This critical vulcanizing rate, relative to the blank mix as unity, has been calculated for each mix from (1) its rate of cure at a fixed temperature, relative to the blank (as shown by the experiments already described) and (2) the difference between this fixed temperature and the blow-out temperature, using a factorial temperature coefficient of 2.35 per 10° C; results are given in Table 2.

Series II was made at a different time from series I, and the blank mixing in the former gives a lower blow-out temperature. Since the other mixings in each series were based on the master-batches from which their respective blanks were drawn, the critical vulcanizing rates have been calculated relative to the respective blanks. Since differences of this magnitude can arise in the blow-out (and hence critical) temperatures of supposedly identical mixings, the results must be accepted with some reserve as giving only approximate critical vulcanizing rates.

All the accelerators improved somewhat the critical vulcanizing rate. Hence some reduction in the vulcanizing period can be obtained, in spite of the lower temperature necessitated by the speeding of the reaction and consequent greater danger of blow-out. The lower temperature also permits saving in fuel. BA is in this respect the most efficient accelerator examined, while DPG, ZPD, and TET do not differ greatly from one another. In both BA and DPG mixings, the use of magnesium oxide further increases the critical vulcanizing rate, but zinc oxide practically destroys the improvement effected by the accelerator alone.

It would be premature to attempt any explanation of how accelerators and metallic oxides alter the critical vulcanizing rate. The fact that such alterations are possible, however, is not surprising because an accelerator that acts only during the nonexothermic (initial and final) stages of the rubber-sulfur reaction would give quicker vulcanization without increased risk of overheating. This example may be a hypothetical or unattainable ideal, but accelerators may exist having at least a tendency in this direction. It indicates, moreover, a possible means of further improvement by developing special accelerators and(or) activators.

ACTIVATION OF SET-CURES

Two series of mixings were made, each comprising a blank and mixings containing (1) zinc oxide 5 parts, (2) magnesium oxide 5 parts, (3) accelerator 1.5 parts, (4) accelerator plus zinc oxide, (5) accelerator plus magnesium oxide. The accelerator in the first series was DPG, and in the second series BA.

Slabs 6 × 6 × 0.1 inch of each mixing were vulcanized for the following periods, no previous moulding being given: 15 and 30 minutes at 141° C (equivalent to 5 and 10 minutes, respectively, at 155° C) and 20, 30, 45, 70, 100, and 150 minutes at 155° C. These periods were chosen so as to cover the initial stages of vulcanization.

The British Standard (B.S.) hardness number[7] of each vulcanizate was measured, and also in a few cases the shear modulus and specific gravity (shear modulus was obtained by a torsion method). An attempt was made to follow the course of vulcanization by each of these properties. Specific gravity did not give any reliable conclusions, owing to the changes being so small. The shear modulus results led to the same conclusions as the hardness results, and as the latter were more complete and accurate, discussion will be confined to them. These results may be studied in two ways: (1) as relative rates of vulcanization at the same temperature; and (2) as relative rates of vulcanization at the critical temperatures (as defined above) for ½-inch thick specimens in open steam. To obtain (2) necessitates the following assumptions: (1) the factorial temperature coefficient of the reaction is 2.35 per 10° C, (2) the relative rates of the reaction in the different mixes are not altered by altering the thickness from 0.1 to ½ inch. The second assumption is approximately true, since by definition the critical temperature corresponds to only a small exothermic temperature rise, and is most nearly true for the surface of the vulcanized sheet, where hardness was measured.

No figures are available for the critical temperature of the mixings containing zinc oxide or magnesium oxide alone, so only the relative rates of vulcanization at the same temperature can be studied in these two cases.

Figures 5 and 6 show B.S. hardness number plotted against (1) period of vulcanization at 155° C, (2) relative period of vulcanization at the respective critical temperatures for ½-inch thick specimens.

In the absence of an organic accelerator, zinc oxide has a slight and magnesium oxide a marked accelerating effect (Figure 5; compare zinc oxide and magnesia mixings with the blank).

Adding zinc oxide to a mixing containing an organic accelerator quickens the early stages of vulcanization, but subsequently it causes little improvement in the BA mxing, and, indeed, retards vulcanization in the DPG mixing when the B.S. hardness number is below 63 (compare DPG and DPG/zinc oxide curves in Figure 5). The initial improvement is thus of little if any value for set-curing, which is required to give a product with a hardness number of about 10 or less. When the mixes are compared at their critical vulcanizing temperatures (Figure 6) the speeds of vulcanization for the mixings with zinc oxide plus accelerator are less than for the corresponding mixings with organic accelerator alone when the hardness number is less than about 50 or 60.

Adding magnesium oxide to the mixings containing either organic accelerator increases the speed of vulcanization (Figure 5). This improvement is still evident when the comparison is made at the critical vulcanizing temperatures (Figure 6).

All four mixings containing an organic accelerator in addition to the metallic oxide vulcanize more quickly than those containing the corresponding metallic oxide alone (Figure 5). Owing to the absence of critical temperature data for the latter mixings, the relative rates of vulcanization at the critical temperatures cannot be compared in this case.

The quickest vulcanization at a fixed temperature is given by the mixings containing DPG plus magnesium oxide and BA plus magnesium oxide; the

next fastest are those containing (1) DPG alone, (2) BA with zinc oxide. At the critical temperature (Figure 6) the mixing containing BA, and magnesium oxide is considerably faster vulcanizing than any of the others, and those containing (1) DPG and magnesium oxide and (2) BA only are the next fastest.

PROPERTIES OF THE FULLY VULCANIZED EBONITES

"Fully vulcanized" means taken to the stage where further vulcanization produces little change in properties. This is roughly 5 hours at 155° C for unaccelerated and 2–3 hours for accelerated mixes, or the equivalent at a lower temperature. The accelerators considered are those listed in Table 1, 1.5 parts being used.

In presence of an accelerator more of the added sulfur combines with the rubber than is possible in its absence. Thus, without an accelerator the free sulfur of a 68:32 rubber-sulfur mix seems never to fall below about 1.55 per cent, whereas in presence of the more active accelerators figures as low as 0.6–0.7 per cent are found. This observation is in keeping with the view suggested by other facts, that the formation of ebonite involves a reversible reaction; the increased ultimate combined sulfur content in presence of an accelerator could thus be explained by its quickening the forward reaction and so displacing the equilibrium.

An important result of the increased combined sulfur is that the plastic yield temperature may be raised 5° C or more. This effect is generally greatest with the most active accelerators. On the other hand, impact strength is reduced by some 15 per cent on the average, as judged by unnotched specimens, though the effect on notched specimens is less. A reduction in impact strength might be expected from the inverse relation generally found between it and resistance to plastic yield.

The 5 parts of metallic oxide added to study activation effects lowered the impact strength further, by 10–20 per cent for zinc oxide and 20–30 per cent for magnesium oxide; this is doubtless the normal weakening effect found with mineral fillers.

Permittivity and power factor, measured at 10^6 cycles per second and 20° C, are not improved by any of the organic accelerators, indeed the power loss is usually somewhat increased (see Table 3). This is not surprising, since accelerators consist of, or may form by decomposition of, substances of a polar nature. It is not possible to trace any relation between the chemical constitution of the accelerator and its effect on power loss, doubtless because of decomposition during vulcanization and, probably, the presence of impurities in the commercial materials. For these reasons the accelerators would not necessarily fall in the same order of merit in commercial mixes containing a variety of more or less reactive ingredients.

Raising the test temperature to 86° C increased the permittivity and power factor by the amounts shown in the righthand columns of Table 3. As would be expected, the ebonite with the lowest yield temperature (unaccelerated mix, 3½-hour vulcanizate; yield temperature 78° C) increases most in power loss, but among the remaining ebonites (yield temperatures 81°–91.5° C) there is no significant relation between these properties. Some of the accelerators, however, appear to improve the electrical properties at elevated temperatures; thus at 86° C the ebonite containing BA has a lower loss factor (5.05) than the 5-hour vulcanizate of the unaccelerated mix (6.45).

The main conclusion is that organic accelerators are generally detrimental to the radio-frequency properties at room temperature, though they may be

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TABLE 3

MIXES WITHOUT METALLIC OXIDE (H64 SERIES)
All mixes contained Rubber 68, Sulfur 32

Accelerator (1.5 parts) and vulcanization at 155° C	At 20° C		Increase at 86° C	
	Permittivity	Power factor (%)	Permittivity	Power factor (%)
Nil, 3½ hours	2.79	0.85	0.21	4.4
Nil, 5 hours	2.81	1.05	0.12	1.15
DPG, 3 hours	2.83	1.03	0.13	0.95
Vulkacit CT, 3 hours	2.86	1.30	0.18	1.50
BA, 3 hours	2.81	1.07	0.13	0.65
ZPD, 3 hours	2.82	1.11	0.15	1.00
Trimene Base, 3 hours	2.85	1.22	0.16	1.20
TET, 3 hours	2.87	1.50	0.20	1.45
MBT, 3 hours	2.81	1.01	0.15	1.15

advantageous for hot conditions. Before an accelerator is put into use in a particular mix, therefore, its effect on these properties at service temperature should be examined in this mix.

Measurements of electrical surface resistivity showed that this is not adversely affected by organic accelerators; there was no evidence that they either promote or retard deterioration in surface resistivity during exposure to light.

Another result of the higher degree of vulcanization attained by accelerated ebonites is that their resistance to swelling by such liquids as benzene is improved. The improvement is shown in a reduction of the rate of absorption, *e.g.*, to one-half or less by one of the more active accelerators (DPG or ZPD); the amount finally absorbed, however, is not appreciably altered. The reduced rate of absorption would be advantageous in uses involving intermittent exposure to a volatile swelling liquid which could dry out during the intervening periods.

MECHANISM OF ACCELERATION

Addition of an accelerator to the mix does not noticeably alter the relationship between combined sulfur content and plastic-yield temperature. This is illustrated in Figure 4, in which yield temperature is plotted against free sulfur for 68:32 rubber-sulfur mixes containing, respectively, no metallic oxide (H64), 5 parts zinc oxide (H65), and 5 parts magnesium oxide (H67), in each case with

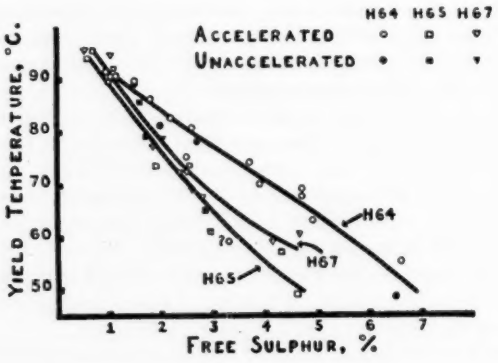

FIG. 4.

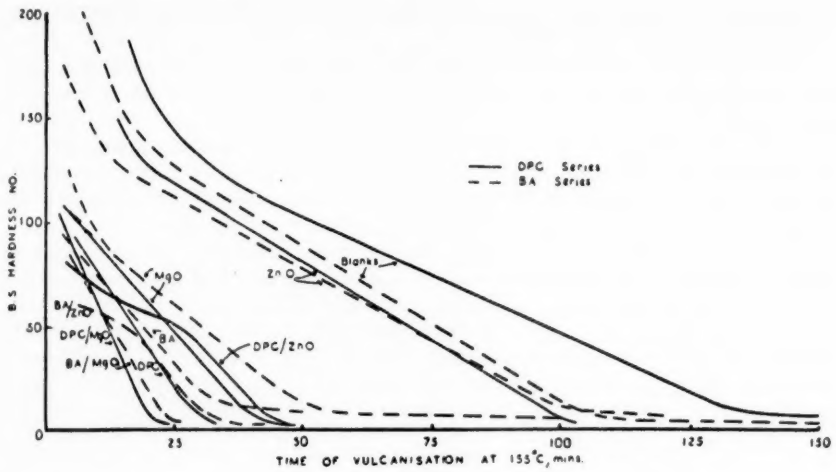

FIG. 5.

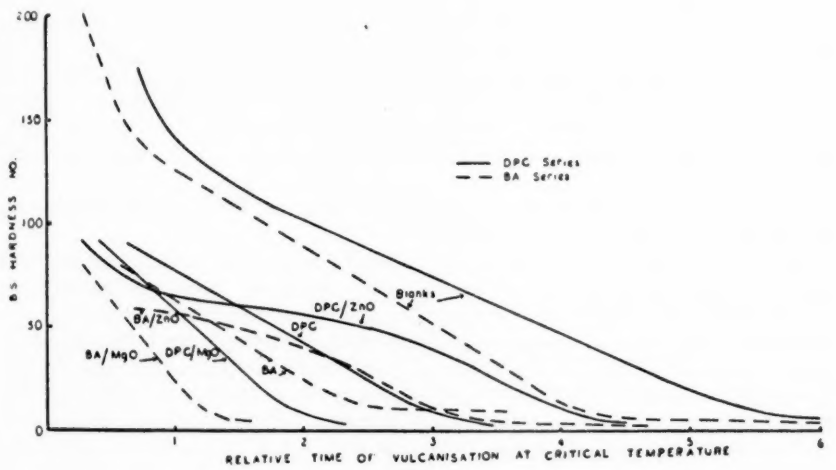

FIG. 6.

and without various accelerators and vulcanized for various periods. In any one series all the points, whether for accelerated or unaccelerated ebonites, lie close to a single curve.

The question whether accelerators make it possible to produce ebonite with less sulfur than is needed in their absence has not been fully studied but the evidence indicates that they do not. Thus, 20 parts of sulfur, with 80 parts rubber, is just sufficient to produce a true ebonite, *i.e.*, a material hard at normal temperatures, without the use of an accelerator. Addition of 10 parts DPG, far from producing a harder vulcanizate, had the opposite effect, the product being still quite flexible after 4 hours at 141° C, even though practically all the sulfur had then combined. The effect of longer vulcanization needs to

be studied, however, since there is evidence that development of ebonitelike characteristics may occur with little increase in combined sulfur[8].

The scanty experimental evidence from the literature supports the view that accelerators do not enable less sulfur to be used[9], although it has been stated that they do.

It has been shown[10] that with unaccelerated rubber-sulfur mixes reducing the vulcanizing temperature, with corresponding lengthening of the vulcanizing periods, leads to higher yield temperatures. The present investigation has shown that this is true of mixes containing organic accelerators.

All the evidence therefore points to the conclusion that the action of an organic accelerator in the formation of ebonite is simply to increase the rate of the rubber-sulfur reaction, in contrast to soft rubber where the relationship between combined sulfur and physical properties is radically altered and the production of a satisfactory vulcanizate with less combined sulfur is made possible. This conclusion agrees with that of Glancy, Wright, and Oon[11], that organic accelerators are simply "regulators" of the rubber-sulfur reaction.

SUMMARY

1. An investigation was made of the influence of several organic accelerators, of the types commonly used in soft rubber, on the vulcanization of ebonite and the properties of the product. This includes the study of zinc and magnesium oxides as activators, and of variation in the proportion of accelerator used.

2. Most of the accelerators are effective in the vulcanization of ebonite, and it is definitely established that they accelerate the final "hard rubber" phase of the rubber-sulfur reaction. The degree of acceleration, however, is much less than in soft rubber, and the different accelerators do not show the same relative efficiencies.

3. Neither zinc oxide nor magnesium oxide functions as an accelerator activator in the hard-rubber reaction.

4. The effects of accelerators and metallic oxides on the maximum safe rate of vulcanization, *i.e.*, consistent with avoiding excessive exothermic temperature rise, have been examined. All the accelerators improved the maximum safe rate of vulcanization; the most effective were butyraldehyde-aniline and diphenylguanidine, the former being considerably the better. Zinc oxide reduced the maximum safe rate when added to an accelerated mixing; magnesium oxide caused a further improvement. Butyraldehyde-aniline plus magnesium oxide was thus the most effective combination for enabling the vulcanizing period to be reduced without risk of overheating due to the exothermic hard-rubber reaction. The fact that certain accelerators or accelerator metallic oxide combinations make possible quicker vulcanization without increased exothermic temperature rise suggests the possibility of developing special ebonite accelerators possessing this useful characteristic in an enhanced degree.

5. For speedy set-curing, a mixing containing either diphenylguanidine or butyraldehyde-aniline with magnesium oxide appears best, particularly the latter, since it can be used at a higher vulcanizing temperature without excessive overheating. The activating effect of zinc oxide in the early (soft-rubber) stage of vulcanization is of no use in speeding up set-curing; indeed, zinc oxide usually delays the formation of a satisfactory set-cured product.

6. Accelerators do not alter the relationship between combined sulfur content and physical properties, as they do in soft rubber; their function is simply

to increase the rate of the rubber-sulfur reaction, and, perhaps as a consequence of this, to enable more of the added sulfur to become combined.

7. The technically important effects of accelerators on the properties of ebonite are: increase in resistance to plastic yield, decrease in impact strength, increase in resistance to swelling liquids, and increase (usually) in dielectric loss at normal temperatures, though the loss at elevated temperatures may be reduced. The first three of these effects result from the more complete combination of sulfur noted above.

REFERENCES

[1] Naunton, *Trans. Inst. Rubber Ind.* **2**, 18 (1926); Glancy, Wright and Oon, *Ind. Eng. Chem.* **18**, 73 (1926); Davies, *Trans. Inst. Rubber Ind.* **9**, 130 (1933); **10**, 76 (1934); *India-Rubber J.* **89**, 51 (1935); Kashin, *J. Rubber Ind. U.S.S.R.* **10**, 521 (1936); Rubber Assoc. Brit. Rubber Manufrs. Information Bur. Circ. No. **223** (1939); Morley, *J. Rubber Research* **16**, 263 (1947).

[2] See particularly Church and Daynes, *J. Rubber Research* **14**, 165 (1945); **15**, 127, 163 (1946).

[3] Glancy, Wright, and Oon, *Ind. Eng. Chem.* **18**, 73 (1926); Kashkin, *J. Rubber Ind. U.S.S.R.* **10**, 521 (1936); Rubber Assoc. Brit. Rubber Manufrs. Information Bur. Circ. No. **223** (1939).

[4] Daynes, *Trans. Inst. Rubber Ind.* **11**, 336 (1935); Church and Daynes, *J. Rubber Research* **13**, 55 (1944).

[5] Davies, *Trans. Inst. Rubber Ind.* **9**, 130 (1933); **10**, 176 (1934).

[6] Morley, *J. Rubber Research* **16**, 263 (1947).

[7] British Standards Institution. British Standard Methods of Testing Vulcanized Rubber. BS903–1940.

[8] Scott, *J. Rubber Research* **17**, 170 (1948).

[9] Glancy, Wright, and Oon, *Ind. Eng. Chem.* **18**, 73 (1926); Stevens, British Patent 269,693; *India-Rubber J.* **73**, 923 (1927); Marchandise, "Encyclopédie du Caoutchouc", Paris, 1929, p. 333; J. M. Steel & Co., Ltd., "Vulkacil-Ct", London (no date).

[10] Church and Daynes, *J. Rubber Research* **16**, 93 (1947).

[11] Glancy, Wright, and Oon, *Ind. Eng. Chem.* **18**, 73 (1926).

XXXV. FURTHER EXPERIMENTS ON THE INFLUENCE OF SULFUR RATIO *

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INTRODUCTION

The influence of varying the sulfur content of a rubber-sulfur ebonite between 28 and 35 per cent has already been studied[1] as part of the Joint Ebonite Research of the Electrical Research Association and R.A.B.R.M. The present continuation of the research deals with a wider range, 21.5 to 50 per cent, with special reference to the plastic yield and oil resistance of the ebonite.

It is generally accepted that resistance to plastic yield is improved by increasing the sulfur ratio, and there is ample evidence that this is true up to 35 per cent. Since reduction of plastic yield is one of the improvements most desired, it is important to know how far it can be effected by still further raising the sulfur ratio.

Oil resistance has been studied because in the electrical industry there has been an impression that ebonite does not resist mineral oils, *e.g.*, transformer oil, at high temperatures[2]. The Joint Research has already shown[3], however, that rubber-sulfur ebonites containing 25.8 per cent or more of combined sulfur are little affected by prolonged immersion (10 weeks) in transformer and paraffin oils at 100° C. The unfavorable impression among users may have arisen from experience of ebonites having a relatively low degree of vulcanization, which, as the present investigation shows, are much inferior in oil resistance, although they may possess, especially if heavily loaded with fillers, the high rigidity suggestive of a well vulcanized material.

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The relationship between degree of vulcanization and oil resistance was, therefore, studied to find how much combined sulfur is necessary to confer satisfactory resistance. These experiments were extended to the high-sulfur ebonites examined for plastic yield.

II. EXPERIMENTAL

MIXINGS AND VULCANIZATION

The mixings examined, and vulcanizing conditions, were as follows:

	H78A	H78B	H78C	H78D	H79A	H81A	H116A	H116B	H116C
Rubber	66.7	73	77	78.5	60	50	60	55	50
Sulfur	33.3	27	23	21.5	40	50	40	45	50
Diphenylguanidine	—	—	—	—	—	—	2.5	2.5	2.5
Vulcanization									
temp. (° C)	155	155	155	155	155	155	148	148	148
time (hours)	2	2	2	2	5	2	4	4	4
	3	3	3	3		3	6	6	6
	5	5	5	5		5			
	8	8	8	8					

During the vulcanization of H81A, sulfur exuded from the edges of the mold, presumably because the amount present was greater than could be dissolved by the rubber, and the finished ebonite contained only 45 per cent sulfur instead of the nominal 50 per cent. (This loss of sulfur did not occur when 40 parts of amorphous silica, Neosyl-C, were added to the mix, probably because the filler adsorbed the excess sulfur.) A smaller loss, 1.1–1.5 per cent, occurred with mixes H116A–C.

TESTING METHODS AND RESULTS

Results for the H78 series are given in Table 1. For the swelling tests, specimens 15 × 15 × 4.5 mm. were immersed in benzene at 25° C, petroleum ether (b.p. 50°–60° C, density 0.67 gram per cc. at 15° C) at 25° C, paraffin lamp oil (density 0.79) at 90° C, and transformer oil (density 0.87) at 100° C. Swelling maximum is expressed as volumes of liquid absorbed by 100 volumes of ebonite; in cases where the maximum was not reached, or there is doubt as to its value, the swelling after a definite period (shown below the name of the liquid) is given in brackets. Swelling times are arbitrary comparative figures, but correspond approximately to the period (hours) required for the swelling to reach half its maximum; where the swelling was very small this time could not be determined.

Plastic yield temperature was determined by the R.A.B.R.M. torsion method[4]; the slope of the temperature/yield curve was about 5–6 degrees (per 10° C) in all cases except the 5- and 8-hour vulcanizates of H78A (9–10 degrees). Young's modulus was measured at room temperature.

Table 2 gives the results for the other mixes obtained by the same methods as above; swelling data relate to benzene at 25° C. A few measurements of impact strength were made also, and are discussed below.

DISCUSSION

Young's modulus.—An interesting and unexpected result shown by Table 1 is that the modulus of the 8-hour vulcanizates is practically constant over a range of sulfur contents from 21.5 to 33.3 per cent. Plotting the modulus

TABLE 1

RESULTS FOR H78

Note: The four lines of figures for each mix relate to 2, 3, 5, and 8-hour vulcanizates, respectively.

Mix and % sulfur	Vulcanization coefficient	Young's modulus (kg. per sq. cm.)	Plastic yield temp. (° C)	Swelling maximum: Benzene	Swelling maximum: Petroleum ether 56 days	Swelling maximum: Paraffin 35 days	Swelling maximum: Transformer oil 28 days	Swelling time: Benzene	Swelling time: Petroleum ether	Swelling time: Paraffin	Swelling time: Transformer oil
D	20.0	300	14	159	—	—	100±	<14	—	—	155
21.5	25.0	2,500	24	—	—	—	50	—	—	—	60
	27.5	17,000	39	128	33	27	9.5	<14	220	35	45
	27.5	24,000	41	126	(26)	18.5	7.5	<14	>370	40	40
C	21.5	700	22	152	—	—	63	<13	—	—	48
23	28.0	3,000	—	124	35	27.5	7.5	10	110	30	42
	30.0	16,000	48	117	(23)	16.5	2(2)	14	>430	45	—
	30.5	25,000	56	111	(16)	12.5	1.5(1.5)	14	>350	43	—
B	19.0	—	—	—	—	—	25.5	—	—	—	42
27	32.5	—	—	102	(12)	17.5	2(2.5)	16	>190	—	—
	36.0	19,000	—	83	(5)	8.5	0.7(0.7)	24	>230	—	—
	37.0	22,000	76	89	(1)	8.0	0.6(0.2)	34	—	32	—
A	33.5	5,000	16	104	—	—	21.5	<13	—	—	60
33.3	43.5	18,000	—	74	(3.2)	3(4)	0.9(0.4)	35	>300	80	—
	46.5	26,000	85	71	(0.3)	(2.5)	0.6(0.6)	90	—	—	—
	47.0	23,000	87	71	(0.2)	(1.7)	0.4(0.2)	120	—	—	—

TABLE 2

RESULTS FOR H79A, H81A, AND H116

Mix and vulcanization	Vulcanization coefficient	Swelling maximum*	Swelling time	Plastic yield†: Yield temp. (° C) (i)	Plastic yield†: Yield temp. (° C) (ii)	Plastic yield†: Slope (degrees per 10° C) (i)	Plastic yield†: Slope (degrees per 10° C) (ii)
H79A							
5 hours	—	52	235	80.5	—	14	—
H81A							
2 hours	50.5	—	—	54	98	6.1	9.3
3 hours	54	—	—	60	103	7.2	7.6
5 hours	55	47	225	74	109	7.2	7.2
H116A							
4 hours	—	—	—	82	—	7	—
6 hours	55.5	53(62)	750	86	—	17±	—
H116B							
4 hours	—	—	—	73.5	—	11	—
6 hours	65	45(56)	620	76.5	—	>8	—
H116C							
4 hours	—	—	—	64	—	20±	—
6 hours	77	38(55)	240	64	—	20±	—

* Values in brackets are corrected for soluble substances extracted during swelling, so as to give the percentage absorption by the rubber-sulfur compound.

† Data under (i) refer to the normal yield point and the slope of the curve immediately above it; those under (ii) relate to the second yield point referred to in the following text.

against vulcanization coefficient (Figure 1) shows that, during the later stages of vulcanization, the modulus increased greatly for a small increase in combined sulfur. Prolonging the vulcanization is thus more effective than increasing the sulfur in producing the high rigidity characteristic of ebonite.

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Impact strength.—The 3- and 5-hour vulcanizates of H81A gave notched impact strengths (R.A.B.R.M. falling-weight test[5]) of 2.1 and 3.1 kg.-cm. per sq. cm., respectively, which are much the same as for ebonites of normal sulfur ratio, *e.g.*, 68:32 rubber-sulfur. Similarly, a 50:50:40 rubber-sulfur-Neosyl C mix (3-hour vulcanization at 155° C) gave 1.2 kg.-cm. per sq. cm., about the same as for a 68:32:40 mix. Increasing the sulfur ratio above the normal thus appears not to reduce impact strength.

Plastic yield.—Figure 2 shows the temperature/yield curves for H81A and also for the 50:50:40 rubber-sulfur-Neosyl C mix (H81B). An interesting feature of these curves is the second yield-point some 30°–40° C above the normal one; the cause of this has not been investigated (Table 2, column (ii), shows this second yield temperature and the slope of the temperature/yield curve above it).

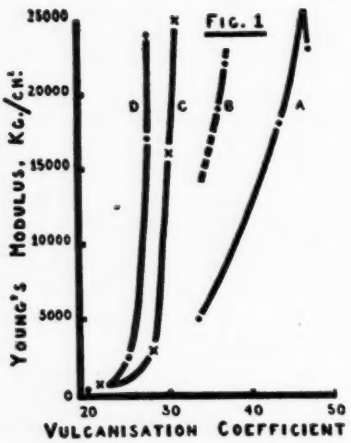

FIG. 1.—Relationship between vulcanization coefficient and Young's modulus (H78A–D). Each curve represents the effect of increasing vulcanizing period.

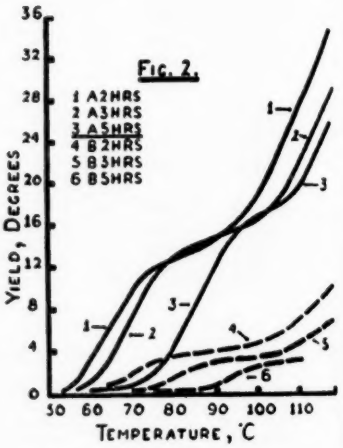

FIG. 2.—Temperature/yield curves (H81A and B).

The data in Table 1, the results for H81A (Table 2), and previous results[6] for both unaccelerated and accelerated ebonites all show that the relation between plastic yield temperature and vulcanization coefficient is somewhat similar to that shown in Figure 1 for Young's modulus, the outstanding features being: (1) prolonged vulcanization is more effective than increased sulfur in producing high yield temperature; and (2) for a given vulcanization coefficient the yield temperature is higher the less sulfur is in the mix.

Figure 3, relating to well vulcanized ebonites of various rubber-sulfur ratios, shows the relation between percentage of sulfur and yield temperature; all available data from this and other investigations are included. With increasing sulfur the yield temperature does not increase continuously, as might have been expected, but shows a maximum at about 35 per cent sulfur. The use of an organic accelerator raises the whole curve.

A possible explanation of the lower yield temperatures of ebonites containing more than 35 per cent sulfur is that the large amount of residual free sulfur lowers the yield temperature by an action analogous to the lowering of the melting point of a crystalline substance by the addition of a second substance.

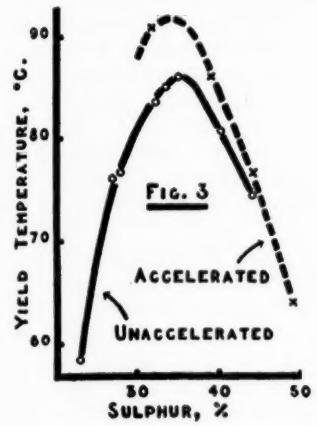

FIG. 3.—Relationship between percentage of sulfur in the mix and yield temperature of the ebonite.

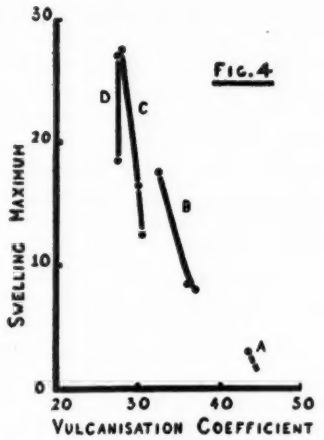

FIG. 4.—Relationship between vulcanization coefficient and swelling maximum in paraffin (H78A–D). Each curve represents the effect of increasing vulcanizing period.

This would also account, qualitatively at least, for the accelerated ebonites showing a higher curve, since they normally contain less free sulfur[7], and for the fact that among ebonites of the same vulcanization coefficient the yield temperature is lower the higher the total (and therefore the free) sulfur content.

Swelling maximum.—Table 1 shows that in benzene the swelling is always large, and increasing the sulfur ratio or vulcanizing period does not alter its order of magnitude. When plotted against vulcanization coefficient all the points lie very nearly on a single curve, showing that prolonging vulcanization is equivalent to increasing the sulfur ratio (very prolonged overvulcanization, however, causes swelling to increase again to a small extent[8].

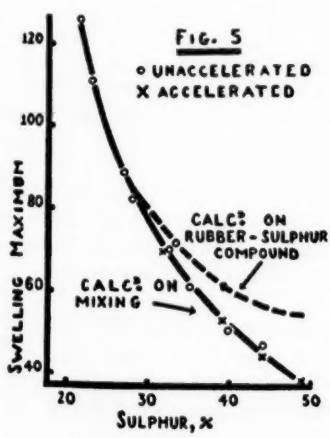

FIG. 5.—Relationship between percentage of sulfur in the mix and swelling maximum (benzene) of the ebonite.

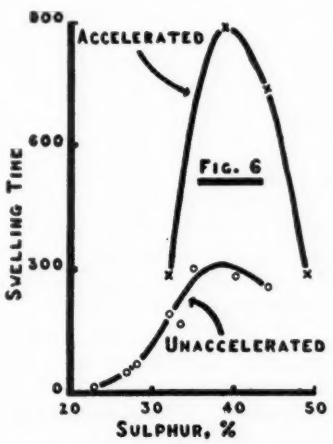

Fig. 6.—Relationship between percentage of sulfur in the mix and swelling time (benzene) of the ebonite.

In petroleum ether the swelling is always smaller, sometimes very much so, and decreases more rapidly with increasing sulfur ratio or vulcanizing period. mixes containing 27 per cent or more of sulfur, when well vulcanized, show good resistance to the lower aliphatic hydrocarbons, such as petroleum ether.

The results for paraffin broadly resemble those for petroleum ether, except that, with increasing vulcanization, the swelling does not decrease to such low values, so only the 33.3 per cent sulfur mix can be said to show satisfactory resistance. Transformer oil is generally similar to petroleum ether and paraffin, but the swelling is less than with the latter, so that mixes with 23 per cent or more of sulfur show satisfactory resistance.

Petroleum ether, paraffin, and possibly transformer oil appear to differ from benzene in one important respect, namely, that sulfur ratio and period of vulcanization affect the swelling/vulcanization coefficient relationship differently. This is evident on plotting swelling against vulcanization coefficient, when it is seen (*e.g.*, in the data for paraffin oil, Figure 4) that a given increase in the coefficient reduces the swelling more if produced by prolonging vulcanization than if produced by adding more sulfur. This is analogous to the effects of these two factors on plastic yield temperature and Young's modulus (see above), and on the swelling time in petroleum ether discussed below.

Figure 5 shows all the available data, from Tables 1 and 2 and elsewhere, for the relation between the swelling maximum (benzene) of well vulcanized ebonites and the percentage of sulfur in the mix. The fact that the points for unaccelerated and accelerated ebonites lie approximately on the same curve confirms the previous observation[7] that accelerators do not radically alter the relation between degree of vulcanization and swelling in benzene.

Swelling time.—Table 1 shows that, in benzene, the swelling time increases with increase in either the sulfur ratio or the vulcanizing period, as observed previously[8]. The same appears to be true of petroleum ether, though the times are greater, indicating slower absorption. Swelling time resembles swelling maximum in that increasing sulfur ratio and vulcanizing period have equivalent effects in the case of benzene, whereas with petroleum ether the vulcanizing period again has the greater effect.

The results for paraffin and transformer oil are more complex, as the swelling time apparently shows a minimum at about 27 per cent sulfur, and with transformer oil the swelling times for the 21.5 and 23 per cent mixes decrease with advancing vulcanization. These features can be explained by the high temperature (90°–100° C) used in these tests, as follows: Among soft vulcanized rubbers, the swelling time (at room temperature) decreases as the degree of vulcanization is increased, whereas with ebonites it increases, so there must be a minimum at an intermediate sulfur ratio, probably between 10 and 20 per cent of the mix. Raising the temperature causes a given type of behavior to be exhibited by a vulcanizate with a higher sulfur ratio[9]. Hence at 90°–100° C the minimum swelling time should occur at a sulfur ratio above the 10–20 per cent range; this agrees with the observation that the minimum corresponds to about 27 per cent sulfur.

It follows also that, at 90°–100° C, the mixes with less sulfur (21.5 and 23 per cent) should resemble soft rubber rather than ebonite in their swelling characteristics, *i.e.*, showing a decreasing swelling time with advancing vulcanization. This is found with transformer oil at 100° C though not definitely with paraffin at 90° C.

Figure 6 shows all the available data for well vulcanized ebonites. The swelling time, like yield temperature, passes through a maximum, in this case at about 39 per cent sulfur. In presence of an accelerator the times are

greater, *i.e.*, absorption is slower, as has been observed previously and ascribed to the more complete combination of the sulfur with the rubber[10]. Here again, as with plastic yield temperature, possibly it is the free sulfur which influences the swelling time, owing to its being soluble in benzene and so facilitating penetration of the liquid into the ebonite.

SUMMARY

1. As the percentage of sulfur in a rubber-sulfur ebonite is progressively increased, the yield temperature rises to a maximum and then falls again. There is thus an optimum proportion of sulfur for producing a heat-resistant ebonite. The cause of the reversion on exceeding this optimum has not yet been studied; it is suggested, though without proof, that it may be due to the large amount of sulfur left uncombined. The swelling time (period required for the swelling in benzene to reach a given fraction of its maximum) likewise passes through a maximum at about the same sulfur ratio, and possibly for the same reason.

2. During prolonged vulcanization ebonite may become much harder and more heat-resistant, with little increase in combined sulfur.

3. Plastic yield temperature, hardness (as measured by Young's modulus), and absorption of petroleum hydrocarbons (petroleum ether, paraffin, transformer oil) are not determined solely by the combined sulfur content of the ebonite, but depend on how this has been attained, *i.e.* on the proportion of sulfur in the mix and the period of vulcanization. Increase of combined sulfur by prolonging vulcanization is more effective in producing the characteristic properties of ebonite (high yield temperature, hardness, resistance to petroleum hydrocarbons) than the same increase brought about by adding more sulfur.

4. In attempting to improve the heat-resistance of unloaded rubber-sulfur ebonites it is useless to increase the proportion of sulfur beyond the maximum now generally used, *i.e.* about 35 per cent of the mix, even when an accelerator is used to promote its combination with the rubber. The fact that ebonite can be made more heat-resistant without increase of combined sulfur, suggests a line along which improvement may be sought.

5. The results confirm the previous observation that well vulcanized ebonite is practically unaffected by oils of the petroleum (aliphatic) type, even at 90°–100° C. The swelling action of such liquids, however, increases rapidly when the degree of vulcanization of the ebonite is reduced. The proportion of combined sulfur needed to confer good swelling resistance varies with the nature of the liquid, but can be deduced from the data recorded. There should be no difficulty in making an ebonite to give satisfactory service, so far as swelling resistance is concerned, in contact with oils, provided these consist of aliphatic hydrocarbons. As, however, aromatic hydrocarbons, *e.g.* benzene, toluene, xylene, have a strong swelling action, equally good resistance cannot be expected towards oils of appreciable aromatic content. Hydrocarbons of the cycloparaffin series (naphthenes) appear to be relatively innocuous[9].

REFERENCES

[1] Church and Daynes, *J. Rubber Research* **14**, 165 (1945); **15**, 127, 163 (1946).
[2] See, for example, Dunton and Muir, *Electrician* **104**, 326 (1930).
[3] Scott, *Trans. Inst. Rubber Ind.* **13**, 109 (1937); *J. Rubber Research* **15**, 179 (1946).
[4] Church and Daynes, *J. Rubber Research* **8**, 41 (1939).
[5] Church and Daynes, *Trans. Inst. Rubber Ind.* **13**, 96 (1937).
[6] Scott, *Trans. Inst. Rubber Ind.* **13**, 109 (1937); Church and Daynes, **14**, 165 (1945); **15**, 127, 163 (1946).
[7] Fisher, Newton, Norman, and Scott, *J. Rubber Research* **17**, 161 (1948).
[8] Scott, *Trans. Inst. Rubber Ind.* **13**, 109 (1937).
[9] Scott, *Trans. Faraday Soc.* **38**, 284 (1942).
[10] Scott, *Trans. Inst. Rubber Ind.* **13**, 109 (1937); Parris and Scott, *J. Rubber Research* **10**, 123 (1941).

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